Nickel-(II) Catalyzed *N*-Formylation and *N*-Acylation of Amines

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1. General information

All reactions were carried out under normal conditions and no any stringent conditions were used. 1N solution prepared from commercially available concentrated hydrochloric acid (35%) during reaction workup and purification. All chemicals were obtained from Aldrich Chemical Co., Alfa Aesar, Spectrochem and TCI Europe and used as received without additional purification. Lab reagent grade solvents were used for extraction and column chromatography purchased from Finar chemicals. The progress of reactions was checked by analytical thin-layer chromatography (TLC Silica gel 60 F_{254} plates). The plates were visualized first with short wavelength UV light followed by iodine or ninhydrin staining solution followed by heating.

Melting points were uncorrected and determined in an open capillary tube. GC-MS Spectra were recorded on Shimadzu QP-Ultra 2010 GC-MS system with MS detector (EI mode, 70 ev) and Rtx-624Sil MS column (30 m, 0.32 mm ID, 1.80 μ). The major signals are quoted in m/z with the relative intensity in parentheses. The method used for analysis an injector temperature 250 °C; ion source temperature 200 °C, interface temperature 260 °C, Column flow 2 mL/min Helium, the column oven temperature : initial temperature (T_0) = 60 °C, hold time (t) = 2 min, ramp = 20 °C/min, final temperature (T_1) = 240 °C, hold time (t) = 9 to 19 min.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker Avance-III 400 MHz and 500 MHz spectrometer using TMS as an internal standard. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.25-7.30 ppm, DMSO-d_6: δ_H = 2.49 ppm). Chemical shifts of the minor rotamer are reported if the signal due to the minor rotamer integrated for at least 0.1 H. Signals due to major rotamer and minor rotamer are labeled as such. Infrared spectra were recorded on a Shimadzu FTIR MIRacle 10 and elemental analysis of C, H and N were performed with a Perkin–Elmer series II CHNS/O Analyzer 2400. X-ray diffraction of ligand (8-hydroxyquinoline), catalyst [$Ni(quin)_2$] and [$NiCl_2.6H_2O$] were carried out with a Rigaku MiniFlex 600 difractometer.

2. General Procedures

2.1. Synthesis of *N*-formamides:

To a mixture of aromatic or aliphatic or heterocyclic amine (0.5 g, 1 equiv), [Ni(quin)$_2$] (5 mol %) and imidazole (3 equiv), *N*, *N*-dimethyl formamide (2.5 mL, 5 Volume) was added. The mixture was refluxed at 150 °C and the progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine or ninhydrin stain. After completion, the mixture was diluted with cold water (10 mL) then filtered the precipitate formed and filtrate was extracted with EtOAc (10 mL). The EtOAc layer was washed with 1M hydrochloric acid (3 X 5 mL). The EtOAc layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to obtain the afforded pure *N*-formyl amine without column purification.

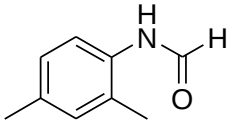
2.2. Synthesis of *N*-acetamides:

To a mixture of aromatic or aliphatic or heterocyclic amine (0.5 g, 1 equiv), [Ni(quin)$_2$] (5 mol %) and imidazole (3 equiv), *N*, *N*-dimethyl acetamide (2.5 mL, 5 Volume) was added. The mixture was refluxed at 150 °C and the progress of the reaction was monitored by TLC visualized with UV short wavelength followed by iodine or ninhydrin stain. After completion, the mixture was diluted with cold water (10 mL) then filtered the precipitate formed and filtrate was extracted with EtOAc (10 mL). The EtOAc layer was washed with 1M hydrochloric acid (3 X 5 mL). The EtOAc layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to obtain pure *N*-formyl amine without column purification.

3. Characterization of products

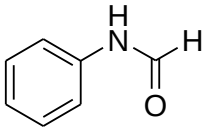
3.1. *N*-formamides (Scheme 2, entries 2a-2u)

_N_-(2,4-dimethylphenyl)formamide (Scheme 2, entry 2a)[1]



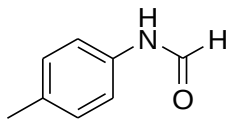
The product was obtained as off-white solid in 96% yield (0.5908 g); **MP:** 112-115 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 65:35): 0.40; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 6/4. Major rotamer: δ 8.45 (d, J = 11.2 Hz, 1H, CHO), 7.85 (br s, 1H, NH), 7.04 (m, 1H, H_{Ar}), 7.01 (m, 2H, H_{Ar}), 2.30 (s, 3H, CH_3), 2.25 (s, 3H, CH_3); Minor rotamer: δ 8.39 (d, J = 1.6 Hz, 1H, CHO), 7.11 (br s, 1H, NH), 7.68 (d, J = 8.8 Hz, 1H, CHO), 7.04 (m, 1H, H_{Ar}), 7.01 (m, 2H, H_{Ar}), 2.28 (s, 3H, CH_3), 2.23 (s, 3H, CH_3); **FTIR (cm^{-1}):** 3454, 3061, 2878, 2735, 2565, 2357, 1910, 1682, 1510, 1468, 1375, 1217, 1121, 1036, 988, 870, 827, 789, 721, 602, 561. **GC-MS (EI, 70ev) *m/z* :** found: 149 ($C_9H_{11}NO$), calculated: 149.19 ($C_9H_{11}NO$).

_N_-phenylformamide (Scheme 2, entry 2b)[2]



The product was obtained as off-white solid in 93% yield (0.6052 g); **MP:** 47-50 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.40; **^{1}H NMR (500 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 5/5. Major rotamer: δ 8.47 (br s, 1H, NH), 8.35 (d, *J* = 2.0 Hz, 1H, CHO), 7.58 (dd, *J* = 8.6, 1.0 Hz, 1H, H_{Ar}), 7.39 – 7.30 (m, 2H, H_{Ar}), 7.17 – 7.09 (m, 2H, H_{Ar}); Minor rotamer: δ 9.19 (br d, *J* = 9.0 Hz, NH), 8.72 (d, *J* = 11.4 Hz, CHO), 7.58 (dd, *J* = 8.6, 1.0 Hz, 1H, H_{Ar}), 7.39 – 7.30 (m, 2H, H_{Ar}), 7.22 – 7.17 (m, 1H H_{Ar}), 7.17 – 7.09 (m, 1H, H_{Ar}); **FTIR (cm^{-1}):** 3013, 2359, 1684, 1601, 1541, 1443, 1396, 1314, 1215, 748, 667; **GC-MS (EI, 70ev) *m/z* :** found: 121 (C_7H_7NO), calculated: 121.14 (C_7H_7NO).

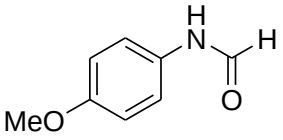
_N_-para-tolylformamide (Scheme 2, entry 2c)[1]



The product was obtained as off-white solid in 95% yield (0.5979 g); **MP:** 50-53 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 5.3/4.7. Major rotamer: δ 8.62 (d, J = 11.6 Hz, 1H, CHO), 8.23 (br s, 1H, NH), 7.12 (d, J = 8.8 Hz, 2H, H_{Ar}), 6.98 (d, J = 8.8 Hz, 2H, H_{Ar}), 2.32 (s, 3H, CH_3); Minor rotamer: δ 8.33 (d, J = 0.8 Hz, 1H, CHO), 7.41 (d, J = 8.4 Hz, 1H, CHO), 7.41 (d, J = 8.4 Hz, 2H, H_{Ar}), 7.14 (d, J = 8.4 Hz, 2H,

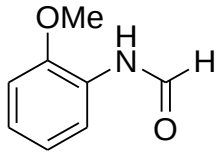
H_{Ar}), 2.31 (s, 3H, CH_3); **FTIR (cm^{-1}):** 3184, 3032, 2916, 2868, 1682, 1616, 1518, 1396, 1298, 1219, 1118, 1042, 937, 883, 806, 640, 598**; GC-MS (EI, 70ev) *m/z* :** found: 135 (C_8H_9NO), calculated: 135.16 (C_8H_9NO).

***N*-(4-methoxyphenyl)formamide (Scheme 2, entry 2d)**[2]



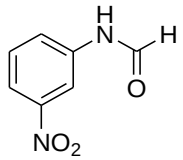
The product was obtained as brown solid in 95% yield (0.5809 g); **MP:** 77-81 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 30:70): 0.40; **^{1}H NMR (500 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 5/5. Major rotamer: δ 8.35 (d, *J* = 1.7 Hz, 1H, CHO), 7.97 (br s, 1H, NH), 7.54 – 7.42 (m, 1H, H_{Ar}), 7.14 – 7.00 (m, 1H, H_{Ar}), 6.98 – 6.83 (m, 2H, H_{Ar}), 3.83 (s, 3H, OCH_3); Minor rotamer: δ 8.52 (d, *J* = 11.5 Hz, 1H, CHO), 7.30 (br s, 1H, NH), 7.54 – 7.42 (m, 1H, H_{Ar}), 7.14 – 7.00 (m, 1H, H_{Ar}), 6.98 – 6.83 (m, 2H, H_{Ar}), 3.81 (s, 3H, OCH_3); **FTIR (cm^{-1}):** 3240, 3049, 2895, 2357, 1653, 1506, 1396, 1233, 1028, 833, 806**; GC-MS (EI, 70ev) *m/z* :** found: 151 ($C_8H_9NO_2$), calculated: 151.16 ($C_8H_9NO_2$).

***N*-(2-methoxyphenyl)formamide (Scheme 2, entry 2e)**[3]



The product was obtained as brown solid in 94% yield (0.5759 g); **MP:** 81-84°C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 30:70): 0.45; Ratio: 6.9/3.1. Major rotamer: δ 8.48 (d, *J* = 1.7 Hz, 1H, CHO), 8.38 (dd, *J* = 8.0, 1.6 Hz, 1H, H_{Ar}), 7.88 (br s, 1H, NH), 7.13 – 7.05 (m, 1H, H_{Ar}), 7.02 – 6.89 (m, 2H, H_{Ar}), 3.91 (s, 3H, OCH_3); Minor rotamer: δ 8.76 (d, *J* = 11.6 Hz, 1H, CHO), 7.75 (br s, 1H, NH), 7.22 (dd, *J* = 7.8, 1.4 Hz, 1H, H_{Ar}), 7.15 (td, *J* = 7.9, 1.5 Hz, 1H, H_{Ar}), 7.02 – 6.89 (m, 2H, H_{Ar}), 3.89 (s, 3H, OCH_3); **FTIR (cm^{-1}):** 3838, 3750, 3244, 2833, 2359, 1694, 1653, 1522, 1456, 1258, 1227, 1028, 864, 739; **GC-MS (EI, 70ev) *m/z* :** found: 151 ($C_8H_9NO_2$), calculated: 151.16 ($C_8H_9NO_2$).

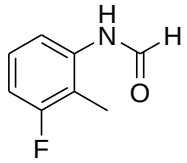
***N*-(3-nitrophenyl)formamide (Scheme 2, entry 2f)**[2]



The product was obtained as yellow solid in 50% yield (0.2985 g); **MP:** 137-139 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 60:40): 0.40; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 7.1/2.9 Major rotamer: δ 8.46 (s, 1H, CHO), 8.39 (t, J = 2.0 Hz, 1H, H_{Ar}), 8.04-7.97 (m, 2H, H_{Ar}), 7.58-7.50 (m, 2H, H_{Ar}), (NH not observed); Minor rotamer: δ 8.80 (d, J = 10.4 Hz,1H, CHO), 8.06 (d, J = 1.2 Hz, 1H,

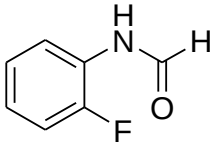
H_{Ar}), 7.58-7.50 (m, 1H, H_{Ar}), 7.40 (dd, J = 8.0 and 1.6 Hz, 1H, H_{Ar}); **FTIR (cm^{-1}):** 3260, 3094, 2847, 2355, 1954, 1661, 1620, 1520, 1433, 1395, 1333, 1261, 1179, 1153, 999, 937, 881, 845, 785, 733, 665; **GC-MS (EI, 70ev) *m/z* :** found: 166 ($C_7H_6N_2O_3$), calculated: 166.13 ($C_7H_6N_2O_3$).

***N*-(3-fluoro-2-methylphenyl)formamide (Scheme 2, entry 2g)**



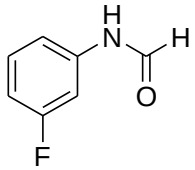
The product was obtained as yellow brown solid in 82% yield (0.5002 g); **MP:** 84-88 °C; **R_F** (eluent hexanes/EtOAc 80:20): 0.50; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 6/4; Major rotamer: δ 8.54 (d, J = 11.2 Hz, 1H, CHO), 7.77 (br s, 1H, NH), 7.20-7.14 (m, 1H, H_{Ar}), 6.98-6.86 (m, 2H, H_{Ar}), 2.20 (d, J = 2.0 Hz, 3H, CH_3); Minor rotamer: δ 8.45 (s, 1H, CHO), 7.71 (d, J = 8.0 Hz, 1H, H_{Ar}), 7.20-7.14 (m, 1H, H_{Ar}), 7.08 (br s, 1H, NH), 6.98-6.86 (m, 1H, H_{Ar}), 2.18 (d, J = 1.6 Hz, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** Major rotamer: 163.60,162.55, 162.11, 127.46, 127.38, 127.16, 127.08, 118.75, 118.72, 116.17, 116.15, 112.83, 112.64, 9.26, 9.22; Minor rotamer: 160.61, 160.17, 159.34, 136.85, 136.80, 136.06, 136.01, 117.55, 117.40, 116.66, 116.52, 112.32, 112.14, 9.17; **FTIR (cm^{-1}):** 3244, 3044, 2980, 2918, 1651, 1585, 1541, 1454, 1288, 1238, 1182, 1072, 1051, 968, 908, 783, 731, 656, 592; **GC-MS (EI, 70ev) *m/z* :** found: 153 (C_8H_8FNO), calculated: 153.15 (C_8H_8FNO).

N-(2-fluorophenyl)formamide (Scheme 2, entry 2h)[3]



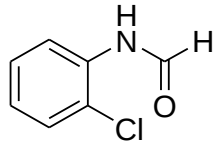
The product was obtained as yellow liquid in 77% yield (0.4798 g); **R_F** (eluent hexanes/EtOAc 80:20): 0.47; **^{1}H NMR (400 MHz, CDCl3):** Mixture of rotamers is observed. Ratio: 6.5/3.5; Major rotamer: δ 8.46 (d, J = 0.8 Hz, 1H, CHO), 8.33 (t, J = 8.0 Hz, 1H, H_{Ar}), 7.51 (br s, 1H, NH), 7.16-7.07(m, 3H, H_{Ar}); Minor rotamer: δ 8.68 (d, J = 11.2 Hz, 1H, CHO), 7.63 (br s, 1H, NH), 7.23-7.21 (m, 1H, H_{Ar}), 7.16-7.07(m, 3H, H_{Ar}); **FTIR (cm^{-1}):** 3734, 3647, 3250, 2874, 2355, 2232, 1682, 1597, 1523, 1456, 1385, 1252, 1177, 1097, 1007, 831, 750, 567; **GC-MS (EI, 70ev) *m/z* :** found: 139 (C_7H_6FNO), calculated: 139.13 (C_7H_6FNO).

***N*-(3-fluorophenyl)formamide (Scheme 2, entry 2i)**[2]



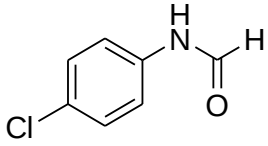
The product was obtained as cream white solid in 85% yield (0.5302 g); **MP:** 56-57°C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 80:20):0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 5.5/4.5; Major rotamer: δ 8.37 (d, J = 1.6 Hz, 1H, CHO), 7.60 (br s, 1H, NH), 7.48(dt, J = 6.0 and 2.0 Hz, 1H, H_{Ar}), 7.34-7.7.24 (m, 1H, H_{Ar}), 6.90-6.83 (m, 2H, H_{Ar}); Minor rotamer: δ 8.71 (d, J = 11.2 Hz, 1H, CHO), 8.54 (br s, 1H, NH), 7.34-7.7.24 (m, 1H, H_{Ar}), 7.17(d, J = 8.0 Hz, 1H, H_{Ar}), 6.90-6.83 (m, 2H, H_{Ar}); **FTIR (cm^{-1}):** 3071, 1686, 1597, 1520, 1474, 1439, 1279, 1236, 1171, 1146, 1032, 982, 841, 677, 646; **GC-MS (EI, 70ev) *m/z* :** found: 139 (C_7H_6FNO), calculated: 139.13 (C_7H_6FNO).

***N*-(2-chlorophenyl)formamide (Scheme 2, entry 2j)**[3]



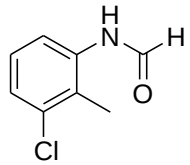
The product was obtained as pale yellow solid in 66% yield (0.4002 g); **MP:** 77-81 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 80:20):0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 6.6/3.4; Major rotamer: δ 8.50 (s, 1H, CHO), 8.45(d, J = 8.0 Hz, 1H, H_{Ar}), 7.67 (br s, 1H, NH), 7.38(d, J = 8.0 Hz, 1H, H_{Ar}), 7.30-7.7.26 (m, 1H, H_{Ar}), 7.09 (t, J = 8.0 Hz, 1H, H_{Ar}); Minor rotamer: δ 8.72 (d, J = 11.2 Hz, 1H, CHO), 7.67 (br s, 1H, NH), 7.43 (d, J = 8.0 Hz, 1H, H_{Ar}), 7.30-7.7.26 (m, 1H, H_{Ar}), 7.15-7.11(m, 1H, H_{Ar}); **FTIR (cm^{-1}):** 3242, 3111, 3044, 2901, 2783, 1703, 1665, 1584, 1526, 1439, 1396, 1298, 1163, 1034, 978, 943, 862, 791, 673, 540; **GC-MS (EI, 70ev) *m/z* :** found: 155 (C_7H_6ClNO), calculated: 155.58 (C_7H_6ClNO).

***N*-(4-chlorophenyl)formamide (Scheme 2, entry 2k)**[4]



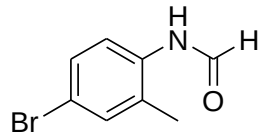
The product was obtained as yellow brown solid in 78% yield (0.4748 g); **MP:** 104-106 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.40; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 5.9/4.1; Major rotamer: δ 8.36 (d, J = 1.2 Hz, 1H, CHO), 8.23 (br s, 1H, NH), 7.50(m, 2H, H_{Ar}), 7.34-7.23 (m, 2H, H_{Ar}); Minor rotamer: δ 8.64 (d, J = 11.6 Hz, 1H, CHO), 7.38 (br s, 1H, NH), 7.34-7.23 (m, 2H, H_{Ar}) 7.04 (m, 2H, H_{Ar}); **FTIR (cm^{-1}):** 3252, 3188, 3116, 3091, 2895, 2787, 2019, 1900, 1666, 1607, 1487, 1396, 1310, 1254, 1171, 1086, 1011, 934, 818, 764, 611; **GC-MS (EI, 70ev) *m/z* :** found: 155 (C_7H_6ClNO), calculated: 155.58 (C_7H_6ClNO).

***N*-(3-chloro-2-methylphenyl)formamide (Scheme 2, entry 2l)**[1]



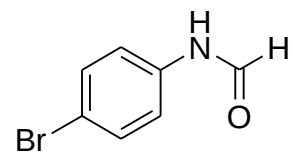
The product was obtained as yellow brown solid in 79% yield (0.4719 g); **MP:** 103-107 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 80:20): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 5.8/4.2; Major rotamer: δ 8.49 (d, J = 11.2 Hz, 1H, CHO), 7.62 (br s, 1H, NH), 7.27 (d, J = 8.0 Hz, 1H, H_{Ar}), 7.15 (t, J = 7.6 Hz, 1H, H_{Ar}), 7.06 (d, J = 8.0 Hz, 1H, H_{Ar}), 2.34 (s, 3H, CH_3); Minor rotamer: δ 8.44 (s, 1H, CHO), 7.76 (d, J = 7.6 Hz, 1H, H_{Ar}), 7.23 (d, J = 7.6 Hz, 1H, H_{Ar}), 7.15 (t, J = 7.6 Hz, 1H, H_{Ar}), 2.33 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** Major rotamer: 163.54, 136.31, 135.82, 128.71, 127.34, 127.18, 119.83, 14.69; Minor rotamer: 159.33, 135.60, 135.02, 127.85, 127.08, 126.72, 122.08, 14.62; **FTIR (cm^{-1}):** 3392, 3240, 3048, 2980, 2835, 2703, 2357, 2330, 1715, 1653, 1603, 1549, 1506, 1454, 1396, 1300, 1233, 1182, 1152, 1111, 1028 1028, 876, 836, 806, 779, 729, 698, 633, 531; **GC-MS (EI, 70ev) *m/z* :** found: 169 (C_8H_8ClNO), calculated: 169.61 (C_8H_8ClNO).

***N*-(4-bromo-2-methylphenyl)formamide (Scheme 2, entry 2m)**



The product was obtained as yellow brown solid in 75% yield (0.4298 g); **MP:** 131-135 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.41; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 5.4/4.6; Major rotamer: δ 8.50 (d, J = 11.6 Hz, 1H, CHO), 7.38-7.32 (m, 2H, H_{Ar}), 7.01 (d, J = 8.4 Hz, 1H, H_{Ar}), 6.94 (br s, 1H, NH), 2.26 (s, 3H, CH_3); Minor rotamer: δ 8.44 (s, 1H, CHO), 7.84 (d, J = 9.2 Hz, 1H, H_{Ar}), 7.38-7.32 (m, 2H, H_{Ar}),2.26 (s, 3H, CH_3); **^{13}C NMR (126 MHz, $CDCl_3$):** Major rotamer: 163.06, 134.04, 133.27, 130.12, 129.84, 124.35, 122.07, 17.61; Minor rotamer: 159.06, 134.12, 133.73, 131.90, 130.52, 119.15, 118.31, 17.57; **FTIR (cm^{-1}):** 3227, 3021, 2893, 1917, 1651, 1530, 1395, 1287, 1190, 1080, 959, 858, 702; **GC-MS (EI, 70ev) *m/z* :** found: 214 (C_8H_8BrNO), calculated: 214.06 (C_8H_8BrNO).

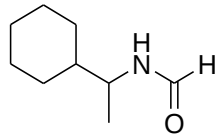
***N*-(4-bromophenyl)formamide (Scheme 2, entry 2n)**[4]



The product was obtained as brown solid in 87% yield (0.5047 g); **MP:** 119-123 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 6.2/3.8; Major

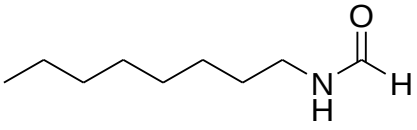
rotamer: δ 8.38 (s, 1H, CHO), 7.48-7.44 (m, 3H, H_{Ar}), 7.22 (br s, 1H, NH), 6.96 (d, J = 8.4 Hz, 1H, H_{Ar}); Minor rotamer: δ 8.64 (d, J = 11.6 Hz, 1H, CHO), 7.73 (br s, 1H, NH), 7.48-7.44 (m, 3H, H_{Ar}), 6.96 (d, J = 8.4 Hz, 1H, H_{Ar}); **FTIR (cm^{-1}):** 3254, 3189, 3111, 3048, 2872, 2361, 1898, 1666, 1587, 1533, 1485, 1393, 1306, 1252, 1067, 1005, 939, 939, 878, 818, 748; **GC-MS (EI, 70ev) *m/z* :** found: 200 (C_7H_6BrNO), calculated: 200.03 (C_7H_6BrNO).

***N*-(1-cyclohexylethyl)formamide (Scheme 2, entry 2o)**[2]



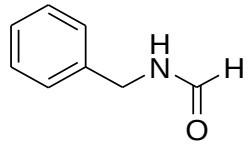
The product was obtained as brown oil in 98% yield (0.5961 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.50; ^{1}H **NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 8.1/1.9; Major rotamer: δ 8.14 (s, 1H, CHO), 5.53 (br s, 1H, NH), 5.47 (s, 1H, CHN), 3.36 (q, J = 6.4 Hz, 2H, CH_2N), 2.16-2.13 (m, 2H, CH_2), 1.98-1.90 (m, 4H, CH_2), 1.70 (m, 1H, CH), 1.64-1.58 (m, 2H, CH_2), 1.55-1.54 (m, 3H, CH_3); Minor rotamer: δ 8.02 (d, J = 15.2 Hz, 1H, CHO), 5.53 (br s, 1H, NH), 5.47 (s, 1H, CHN), 3.28 (q, J = 6.6 Hz, 2H, CH_2N), 2.16-2.13 (m, 2H, CH_2), 1.98-1.90 (m, 4H, CH_2), 1.70 (m, 1H, CH), 1.64-1.58 (m, 2H, CH_2), 1.55-1.54 (m, 3H, CH_3); **FTIR (cm^{-1}):** 3273, 3049, 2932, 2857, 2357, 2232, 1651, 1531, 1449, 1381, 1231, 1067, 891, 729, 531; **GC-MS (EI, 70ev) *m/z* :** found: 155 ($C_9H_{17}NO$), calculated: 155.24 ($C_9H_{17}NO$).

***N*-octylformamide (Scheme 2, entry 2p)**[5]



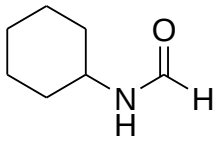
The product was obtained as yellow brown oil in 98% yield (0.5959 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed; Ratio: 7.8/2.2; Major rotamer: δ 8.15 (s, 1H, CHO), 5.55 (br s, 1 H, NH), 3.28 (q, J = 6.8 Hz, 2H, NCH_2), 1.54-1.47 (m, 2H, CH2), 1.28-1.25 (m, 10H, CH2), 0.86 (t, J = 6.8 Hz, 3H, CH_3); Minor rotamer: δ 8.03 (d, J = 12 Hz, 1H, CHO), 5.55 (br s, 1 H, NH), 3.19 (q, J = 6.8 Hz, 2H, NCH_2), 1.54-1.47 (m, 2H, CH2), 1.28-1.25 (m, 10H, CH2), 0.86 (t, J = 6.8 Hz, 3H, CH_3);; **FTIR (cm^{-1}):** 3725, 3275, 3048, 2926, 2857, 2355, 2234, 1659, 1533, 1456, 1383, 1234, 729; **GC-MS (EI, 70ev) *m/z* :** found: 157 ($C_9H_{19}NO$), calculated: 157.25 ($C_9H_{19}NO$).

***N*-benzylformamide (Scheme 2, entry 2q)**[2]



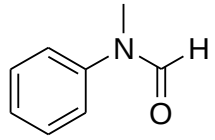
The product was obtained as white solid in 99% yield (0.6225 g); **MP:** 60-63 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed; Ratio: 8.15/1.5; Major rotamer: δ 8.23 (s, 1H, CHO), 7.38-7.22 (m, 5H, H_{Ar}), 6.05 (br s, 1 H, NH), 4.46 (d, J = 6.0 Hz, 2H, NCH_2); Minor rotamer: δ 8.14 (d, J = 6.0 Hz, CHO), 7.38-7.22 (m, 5H, H_{Ar}), 6.05 (br s, 1 H, NH), 4.39 (d, J = 6.4 Hz, 2H, NCH_2); **FTIR (cm^{-1}):** 3271, 3028, 2359, 2234, 1651, 1530, 1389, 1225, 972, 833, 696, 610; **GC-MS (EI, 70ev) *m/z* :** found: 135 (C_8H_9NO), calculated: 135.16 (C_8H_9NO).

***N*-cyclohexylformamide (Scheme 2, entry 2r)**[2]



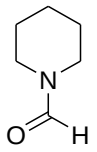
The product was obtained as brown oil in 98% yield (0.6271 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed. Ratio: 7.5/2.5; Major rotamer: δ 8.09 (s, 1H, CHO), 5.47 (br s, 1 H, NH), 3.89- 3.80 (m, 1H, CHN), 1.94-1.90 (m, 2H, CH2), 1.74-1.67 (m, 2H, CH2), 1.63-1.58 (m, 1H, CH2), 1.40 -1.10 (m, 5H, CH2); Minor rotamer: δ 8.12 (s, 1H, CHO), 5.67 (br s, 1H, NH), 3.89-3.80 (m, 1H, CHN), 1.94-1.90 (m, 2H, CH2), 1.74-1.67 (m, 2H, CH2), 1.63-1.58 (m, 1H, CH2), 1.40-1.10 (m, 5H, CH2); **FTIR (cm^{-1}):** 3262, 3048, 2930, 2855, 2357, 2235, 1651, 1531, 1450, 1383, 1252, 1150, 1065, 937, 891, 843, 729; **GC-MS (EI, 70ev) *m/z* :** found: 127 ($C_7H_{13}NO$), calculated: 127.18 ($C_7H_{13}NO$).

N-methyl-N-phenylformamide (Scheme 2, entry 2s)[4]



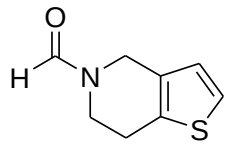
The product was obtained as yellow brown liquid in 85% yield (0.5346 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.46 (s, 1H, CHO), 7.41 (dd, J = 8.0 and 2.0 Hz, 2H, H_{Ar}), 7.27 (d, J = 7.2 Hz, 1H, H_{Ar}), 7.17 (d, J = 7.6 Hz, 2H, H_{Ar}), 2.31 (s, 3H, N-CH_3); **FTIR (cm^{-1}):** 3213, 3051, 2357, 1661, 1595, 1497, 1443, 1352, 1273, 1116, 1053, 978, 824, 760, 696; **GC-MS (EI, 70ev) *m/z* :** found: 135 (C_8H_9NO), calculated: 135.16 (C_8H_9NO).

Piperidine-1-carbaldehyde (Scheme 2, entry 2t)[2]



For this compound, instead of aqueous work-up, DMF was evaporated and the residues were subjected to column chromatography using silica gel (100-200 mesh). Evaporation of eluates afforded the pale yellow liquid in 95% yield (0.6297 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 20:80): 0.35; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.99 (s, 1H, CHO), 3.50 – 3.45 (m, 2H, CH_2N), 3.33 – 3.28 (m, 2H, CH_2N), 1.71 – 1.64 (m, 2H, CH_2), 1.61 – 1.50 (m, 4H, CH_2); **FTIR (cm^{-1}):** 3736, 3242, 3184, 3105, 2997, 2359, 1713, 1680, 1597, 1520, 1456, 1362, 1298, 1269, 1221, 1177, 1150, 818, 775, 729, 698; **GC-MS (EI, 70ev) *m/z* :** found: 113 ($C_6H_{11}NO$), calculated: 113.16 ($C_6H_{11}NO$).

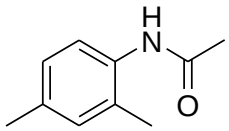
6,7-dihydrothieno[3,2-c]pyridine-5(4H)-carbaldehyde (Scheme 2, entry 2u)



The product was obtained as yellow oil in 97% yield (0.5808 g); $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** Mixture of rotamers is observed; Ratio: 6.2/3.6; Major rotamer: δ 8.18 (s, 1H, CHO), 7.15-7.14 (m, 1H, H_{Ar}), 6.79-6.77 (m, 1H, H_{Ar}), 4.59 (s, 2H, NCH_2), 3.68 (t, J = 11.2 Hz, 2H, NCH2), 2.93-2.84 (m, 2H, CH2); Minor rotamer: δ 8.22 (s, 1H, CHO), 7.15-7.14 (m, 1H, H_{Ar}), 6.79-6.77 (m, 1H, H_{Ar}), 4.46 (s, 2H, NCH_2), 3.85 (t, J = 12.0 Hz, 2H, NCH2), 2.93-2.84 (m, 2H, CH2); **^{13}C NMR (126 MHz, $CDCl_3$):** Major rotamer: 161.87, 125.02, 124.37, 123.87, 123.86, 43.76, 40.67, 25.86; Minor rotamer: 161.50, 133.87, 132.23, 130.80, 130.76, 45.83, 38.01, 24.46; **FTIR (cm^{-1}):** 3283, 3252, 3186, 3113, 3049, 2872, 2355, 1668, 1587, 1531, 1485, 1456, 1393, 1308, 1252, 1177, 1148, 1069, 1005, 878, 818, 760; **GC-MS (EI, 70ev) *m/z* :** found: 167 (C_8H_9NOS), calculated: 167.23 (C_8H_9NOS).

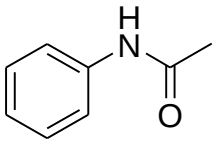
3.2. *N*-acetamides (Scheme 3, entries 1-14)

_N_-(2,4-dimethylphenyl)acetamide (Scheme 3, entry 3a)[1]



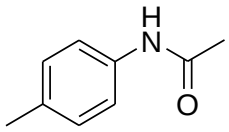
The product was obtained as off-white solid in 95% yield (0.6381 g); **MP:** 104-106 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.55; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 8.6 Hz, 1H, H_{Ar}), 7.03 (m, 2H, H_{Ar}), 7.03 (m, 1H, NH), 2.31 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.20 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3736, 3267, 3011, 2359, 2234, 1651, 1526, 1369, 1248, 1038, 974, 812, 706, 610; **GC-MS (EI, 70ev) *m/z*:** found: 163 ($C_{10}H_{13}NO$), calculated: 163.22 ($C_{10}H_{13}NO$).

_N_-phenylacetamide (Scheme 3, entry 3b)[6]



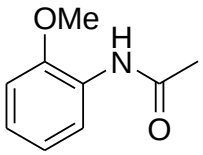
The product was obtained as off-white solid in 91% yield (0.6589 g); **MP:** 112-115 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.45; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, 2H, H_{Ar}), 7.30 (t, J = 7.6 Hz, 2H, H_{Ar}), 7.30 (t, J = 7.6 Hz, 1H, NH), 7.09 (t, J = 7.6 Hz, 1H, H_{Ar}), 2.16 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3289, 3198, 3122, 3059, 1713, 1661, 1597, 1556, 1487, 1366, 1319, 1261, 1180, 1080, 1040, 1013, 967, 839, 748, 692, 606; **GC-MS (EI, 70ev) *m/z* :** found: 135 (C_8H_9NO), calculated: 135.16 (C_8H_9NO).

_N_-p-tolylacetamide (Scheme 3, entry 3c)[1]



The product was obtained as pale yellow solid in 91% yield (0.6317 g); **MP:** 150-153 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 70:30): 0.47; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.39 (d, *J* = 8.4 Hz, 2H, H_{Ar}), 7.35 (br s, 1H, NH), 7.13 (d, *J* = 8.2 Hz, 2H, H_{Ar}), 2.33 (s, 3H, Ar-CH_3), 2.18 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3227, 2359, 1713, 1656, 1522, 1438, 1387, 1279, 1148, 1016, 910, 770, 702; **GC-MS (EI, 70ev) *m/z:*** found: 149 ($C_9H_{11}NO$), calculated: 149.19 ($C_9H_{11}NO$).

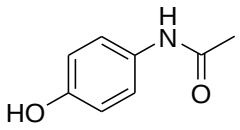
_N_-(2-methoxyphenyl)acetamide (Scheme 3, entry 3d)[1]



The product was obtained as dark brown solid in 95% yield (0.6357 g); **MP:** 69-73 °C; $\mathbf{R_F}$ (eluent hexanes/EtOAc 40:60): 0.40; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.38 (dd, *J* = 8.0, 1.4 Hz, 1H, H_{Ar}), 7.78 (br s, 1H, NH), 7.06 (td, *J* = 7.9, 1.5 Hz, 1H, H_{Ar}), 6.98 (td, *J* = 7.7, 1.2 Hz, 1H, H_{Ar}), 6.90 (dd, *J* = 8.1, 1.0 Hz, 1H, H_{Ar}), 3.91 (s, 3H, OCH_3), 2.23 (s, 3H, CH_3, CO-CH_3); **FTIR (cm^{-1}):** 3252, 2893, 2357, 1715, 1653,

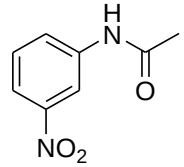
1601, 1541, 1456, 1368, 1288, 1250, 1117, 1024, 1024, 964, 856, 748, 702, 606; **GC-MS (EI, 70ev) *m/z* :** found: 165 ($C_9H_{11}NO_2$), calculated: 165.19 ($C_9H_{11}NO_2$).

***N*-(4-hydroxyphenyl)acetamide (Scheme 3, entry 3e)**[7]



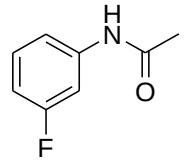
For this compound, instead of aqueous work-up, DMF was evaporated and the residues were subjected to column chromatography using silica gel (100-200 mesh). Evaporation of eluates afforded the white powder 95% yield (0.6559 g); **MP:** 169-173 °C; **R_F** (eluent hexanes/EtOAc 50:50): 0.55; **^{1}H NMR (500 MHz, DMSO-d6):** δ 9.65 (s, 1H, OH), 9.14 (br s, 1H, NH), 7.37 – 7.31 (m, 2H, H_{Ar}), 6.70 – 6.65 (m, 2H, H_{Ar}), 1.98 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3318, 3157, 2355, 2235, 1651, 1541, 1435, 1225, 968, 835, 681; **GC-MS (EI, 70ev) *m/z*:** found: 151 ($C_8H_9NO_2$), calculated: 151.16 ($C_8H_9NO_2$).

***N*-(3-nitrophenyl)acetamide (Scheme 3, entry 3f)**[8]



The product was obtained as yellow solid in 53% yield (0.3449 g); **MP:** 104-106 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.55; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.37 (s, 1H, H_{Ar}), 7.99 (d, *J* = 6.4 Hz, 2H, H_{Ar}), 7.52 (t, *J* = 8.1 Hz, 1H, H_{Ar}), 7.46 (br s, 1H, NH), 2.27 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3254, 2357, 1670, 1526, 1368, 1350, 1078, 1016, 885, 804, 739; **GC-MS (EI, 70ev) *m/z:*** found: 180 ($C_8H_8N_2O_3$), calculated: 180.16 ($C_8H_8N_2O_3$).

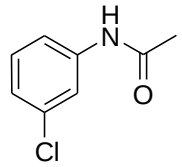
***N*-(3-fluorophenyl)acetamide (Scheme 3, entry 3g)**[8]



The product was obtained as cream white solid in 75% yield (0.5159 g); **MP:** 86-90 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.50;

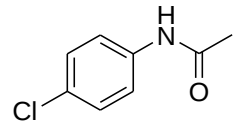
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (br s, 1H, NH), 7.50 (dt, *J* = 10.9, 2.1 Hz, 1H, H_{Ar}), 7.27 (dt, *J* = 14.7, 4.0 Hz, 1H, H_{Ar}), 7.15 (dd, *J* = 8.1, 0.8 Hz, 1H, H_{Ar}), 6.82 (td, *J* = 8.3, 1.9 Hz, 1H, H_{Ar}), 2.20 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3261, 2354, 1665, 1545, 1427, 1337, 1266, 1038, 978, 861, 681; **GC-MS (EI, 70ev) *m/z* :** found: 153 (C_8H_8FNO), calculated: 153.15 (C_8H_8FNO).

***N*-(3-chlorophenyl)acetamide (Scheme 3, entry 3h)**[6]



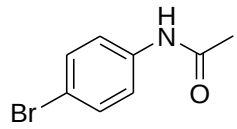
The product was obtained as pale yellowish-brown solid in 87% yield (0.5775 g); **MP:** 74-77 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.50; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.90 (br s, 1H, NH), 7.65 (t, *J* = 1.9 Hz, 1H, H_{Ar}), 7.36 (dd, *J* = 8.1, 1.0 Hz, 1H, H_{Ar}), 7.23 (t, *J* = 8.1 Hz, 1H, H_{Ar}), 7.09 (dd, *J* = 8.0, 0.9 Hz, 1H, H_{Ar}), 2.19 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3254, 2357, 1670, 1539, 1418, 1368, 1279, 1090, 997, 868, 771, 679; **GC-MS (EI, 70ev) *m/z* :** found: 169 (C_8H_8ClNO), calculated: 169.61 (C_8H_8ClNO).

***N*-(4-chlorophenyl)acetamide (Scheme 3, entry 3i)**[6]



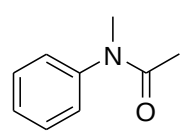
The product was obtained as pale brown solid in 75% yield (0.4983 g); **MP:** 175-178 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.51; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 7.30 (d, *J* = 8.8 Hz, 2H, H_{Ar}), 7.25 (br s, 1H, NH), 2.20 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3252, 2361, 1717, 1668, 1541, 1364, 1260, 1136, 964, 783, 760; **GC-MS (EI, 70ev) *m/z* :** found: 169 (C_8H_8ClNO), calculated: 169.61 (C_8H_8ClNO).

***N*-(4-bromophenyl)acetamide (Scheme 3, entry 3j)**[1]



The product was obtained as pale yellowish-brown solid in 84% yield (0.5213 g); **MP:** 166-170 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.55; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.51 – 7.34 (m, 4H, H_{Ar}), 7.51 – 7.34 (m, 1H, NH), 2.19 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3291, 2359, 1668, 1531, 1393, 1364, 1256, 1070, 1009, 816, 739, 604; **GC-MS (EI, 70ev) *m/z:*** found: 214 (C_8H_8BrNO), calculated: 214 (C_8H_8BrNO).

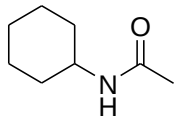
***N*-methyl-*N*-phenylacetamide (Scheme 3, entry 3k)**[9]



The product was obtained as yellow solid in 76% yield (0.5295 g); **MP:** 98-101 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.47; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43 (t, *J* = 7.6 Hz, 2H, H_{Ar}), 7.35 (t, *J* = 7.4 Hz, 1H, H_{Ar}), 7.20 (d, *J*

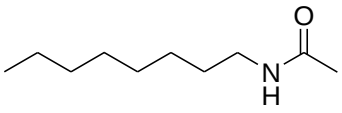
= 7.3 Hz, 2H, H_{Ar}), 3.28 (s, 3H, N-CH_3), 1.89 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3239, 2365, 1659, 1572, 1463, 1339, 1253, 1121, 1067, 982, 827, 757, 656; **GC-MS (EI, 70ev) *m/z* :** found: 149 ($C_9H_{11}NO$), calculated: 149.19 ($C_9H_{11}NO$).

***N*-cyclohexylacetamide (Scheme 3, entry 3l)**[10]



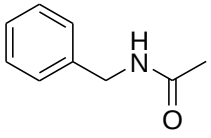
The product was obtained as off-white solid in 98% yield (0.6972 g); **MP:** 100-103 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.45; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 5.42 (br s, 1H, NH), 3.83 – 3.71 (m, 1H, NCH), 1.97 (s, 3H, CO-CH_3), 1.96 – 1.90 (m, 2H, CH_2), 1.71 (ddd, *J* = 10.3, 7.0, 3.3 Hz, 2H, CH_2), 1.67 – 1.58 (m, 1H, CH_2), 1.43 – 1.32 (m, 2H, CH_2), 1.22 – 1.06 (m, 3H, CH_2); **FTIR (cm^{-1}):** 3272, 2362, 1667, 1539, 1457, 1355, 1257, 1134, 1062, 967, 871, 853, 735; **GC-MS (EI, 70ev) *m/z* :** found: 141 ($C_8H_{15}NO$), calculated: 141.21 ($C_8H_{15}NO$).

***N*-octylacetamide (Scheme 3, entry 3m)**[11]



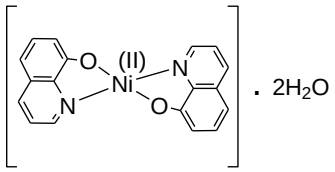
The product was obtained as colourless in 98% yield (0.5600 g); **R_F** (eluent hexanes/EtOAc 70:30): 0.55; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 5.83 (s, 1H, NH), 3.22 (dd, *J* = 13.2, 7.0 Hz, 2H, NCH_2), 1.97 (s, 3H, CO-CH_3), 1.58 – 1.42 (m, 2H, CH_2), 1.28 (dd, *J* = 15.7, 5.5 Hz, 10H, CH_2), 0.87 (t, *J* = 6.9 Hz, 3H, CH_3); **FTIR (cm^{-1}):** 3225, 2358, 1652, 1537 1451, 1371, 1241, 730; **GC-MS (EI, 70ev) *m/z* :** found: 171 ($C_{10}H_{21}NO$), calculated: 171.28 ($C_{10}H_{21}NO$).

***N*-benzylacetamide (Scheme 3, entry 3n)**[12]



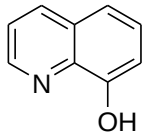
The product was obtained as off-white solid in 98% yield (0.6811 g); **MP:** 59-63 °C; **R_F** (eluent hexanes/EtOAc 70:30): 0.53; **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.38 – 7.32 (m, 2H, H_{Ar}), 7.32 – 7.26 (m, 3H, H_{Ar}), 6.04 (s, 1H, NH), 4.43 (d, *J* = 5.7 Hz, 2H, CH_2), 2.02 (s, 3H, CO-CH_3); **FTIR (cm^{-1}):** 3233, 2363, 1709, 1685, 1576, 1507, 1451, 1358, 1229, 1181, 1145, 834, 757, 709; **GC-MS (EI, 70ev) *m/z:*** found: 149 ($C_9H_{11}NO$), calculated: 149.19 ($C_9H_{11}NO$).

4. Synthesis and characterization of catalyst [Ni(quin)$_2$]



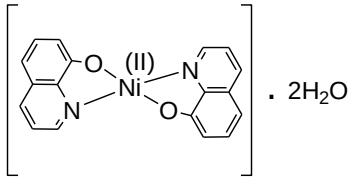
8-hydroxyquinoline (1.22 g, 2 equiv) dissolved in 20 mL ethanol was added to nickel (II) chloride hexahydrate (1 g, 1 equiv) in 3 mL water and the contents were allowed to stir overnight. The precipitated solid were filtered and washed with distilled water followed by 80% Ethanol, dried in air. After drying we get afforded yellow green coloured powder of [Ni(quin)$_2$].2H$_2$O with 70% yield.

8-Hydroxyquinoline (Ligand)



The product is faint yellow powder; MP: 72-74 °C; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 9.84 (s, 1H, OH), 8.84 (dd, J = 4.4 and 1.6 Hz, 1H, H$_{Ar}$), 8.31 (dd, J = 8.4 and 1.6 Hz, 1H, H$_{Ar}$), 7.54 (dd, J = 8.4 and 4.4 Hz, 1H, H$_{Ar}$), 7.46-7.37 (m, 2H, H$_{Ar}$); 7.09 (dd, J = 7.6 and 1.2 Hz, 1H, H$_{Ar}$); **FTIR (cm^{-1}):** 3121, 3044, 2532, 2467, 2355, 1908, 1578, 1497, 1407, 1378, 1273, 1202, 1165, 1094, 1059, 974, 897, 816, 779, 741, 708, 637, 575, 542; **XRD (2θ Values, deg.):** 12.66, 14.26, 15.70, 18.94, 20.06, 23.60, 24.94, 25.98, 28.22, 31.34, 37.96, 44.02, 46.68, 47.40.

[Ni(quin)$_2$] catalyst



The product is yellow green powder; MP: above 280 °C; **^{1}H NMR (400 MHz, DMSO-d6):** There is no any major peak observed in ^{1}H NMR in the aromatic region; **FTIR (cm^{-1}):** 3184, 3055, 2326, 1688, 1643, 1576, 1499, 1464, 1423, 1371, 1323, 1283, 1240, 1107, 1034, 953, 914, 854, 820, 783, 743, 673, 642, 606; **Elemental Analysis (C, H, N; Percent by Weight):** C$_{18}$H$_{12}$NiN$_2$O$_2$·2H$_2$O (383.02): calcd. C = 56.44, H = 4.21, N = 7.31; found C = 55.10, H = 4.12, N = 7.15; **XRD (2θ Values, deg.):** 7.00, 8.90, 9.74, 10.82, 16.70, 18.40, 21.08, 23.16, 24.90, 25.84, 29.36, 33.13, 35.5, 36.54, 38.00, 40.64, 41.66, 42.88, 44.60, 47.12, 51.26.

Nickel (II) chloride hexahydrate [NiCl$_2$.6H$_2$O]

XRD (2θ Values, deg.): 16.48, 18.86, 26.70, 35.54, 41.54, 44.90, 46.24, 49.32, 70.98.

5. References

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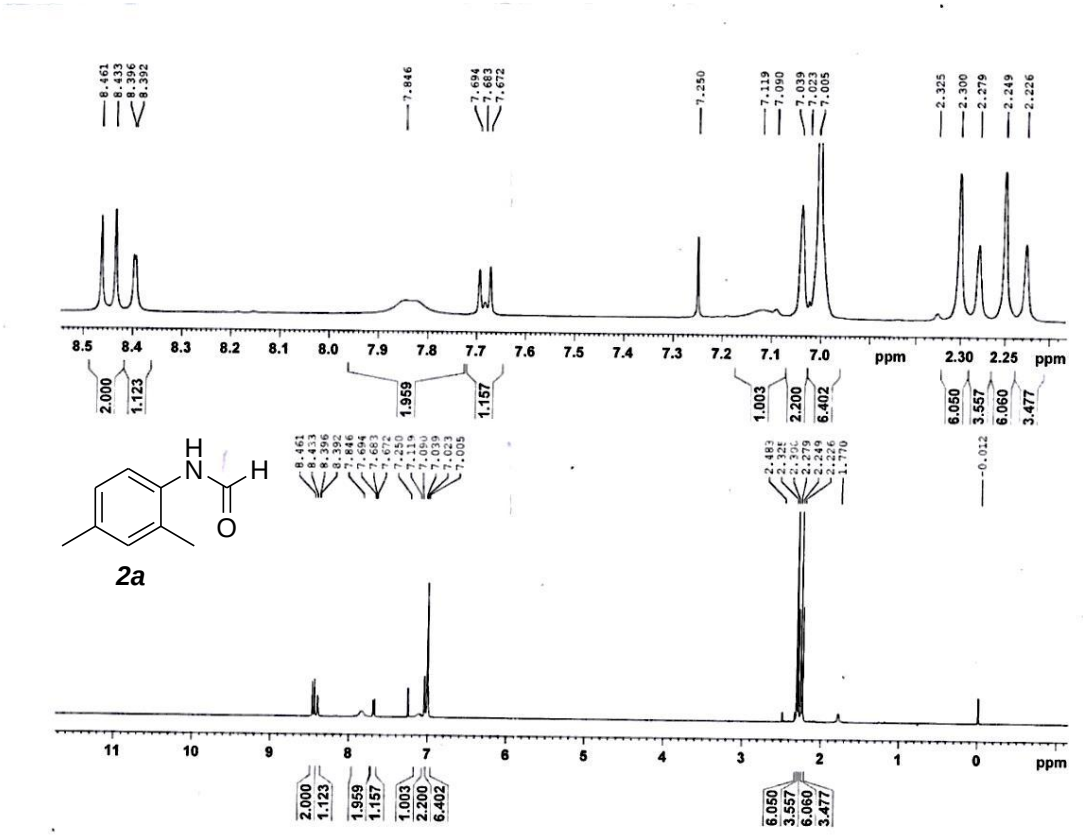
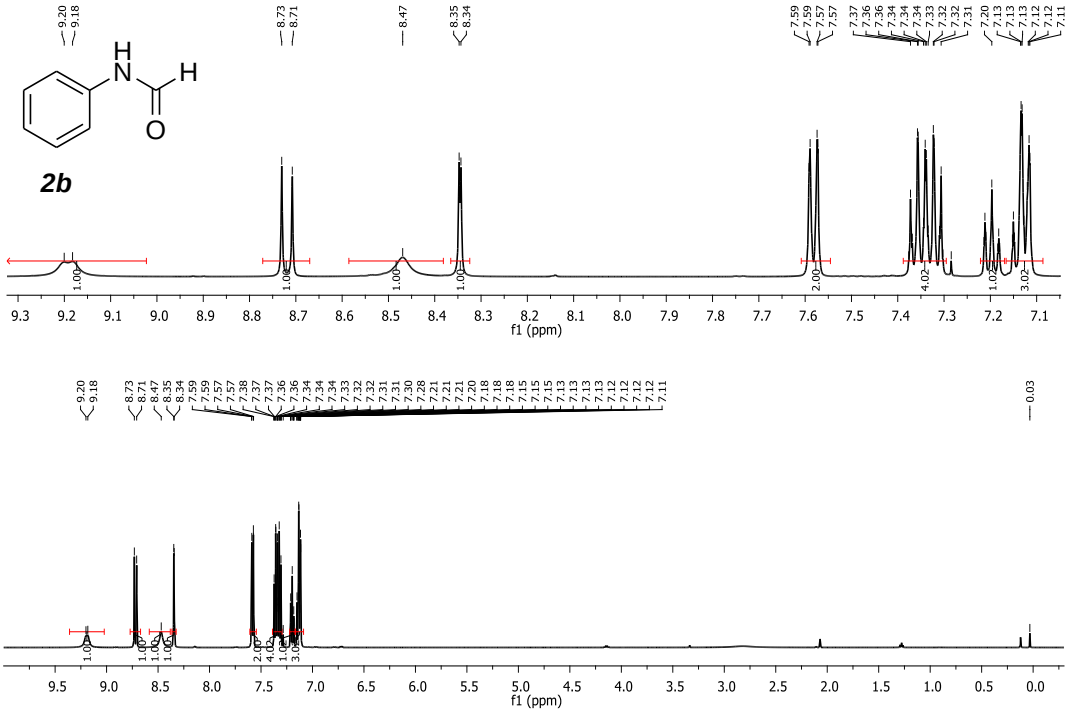
6. ^{1}H NMR and ^{13}C NMR spectra

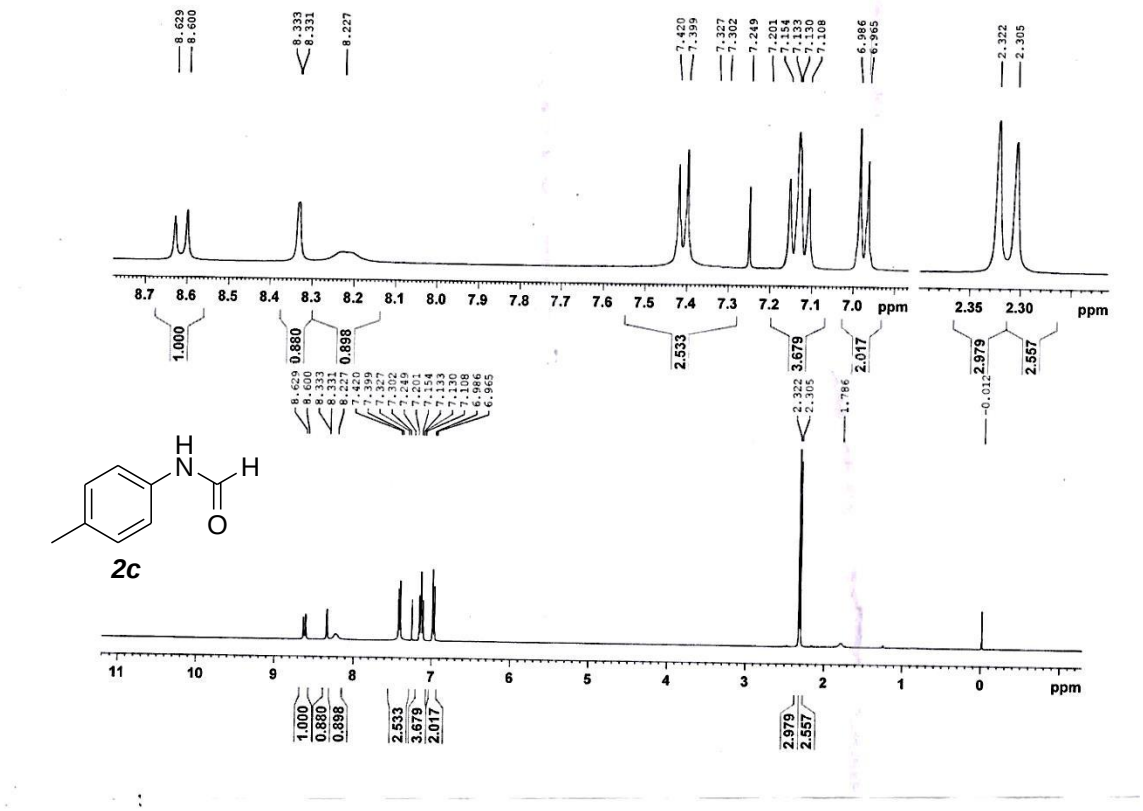
(Scheme 2, entry 2a)



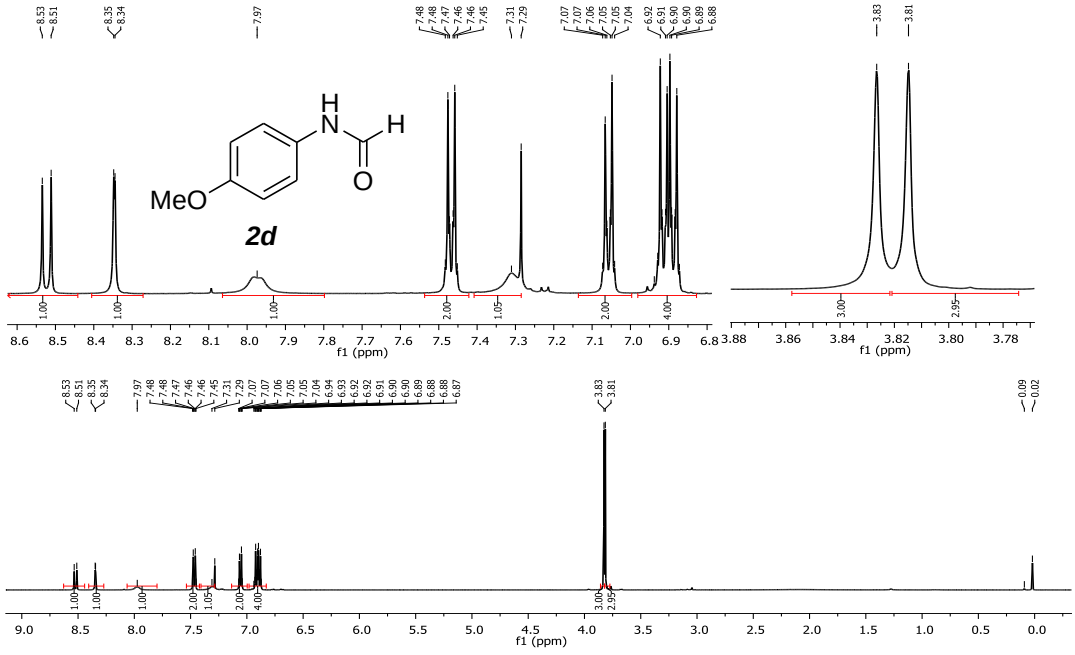
(Scheme 2, entry 2b)



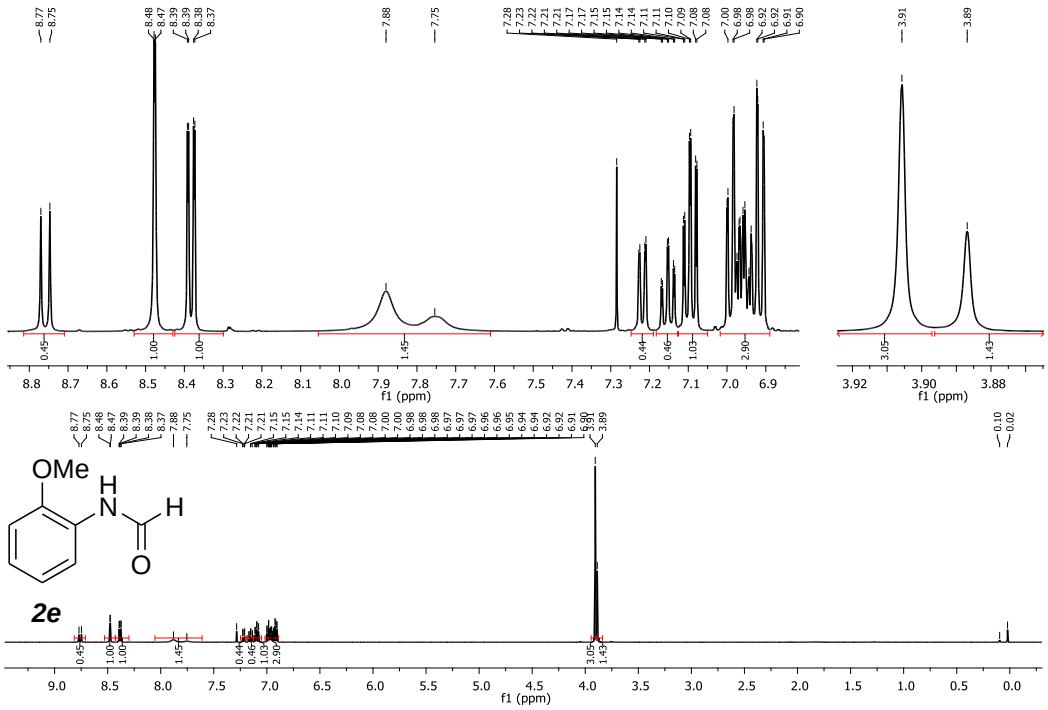
(Scheme 2, entry 2c)



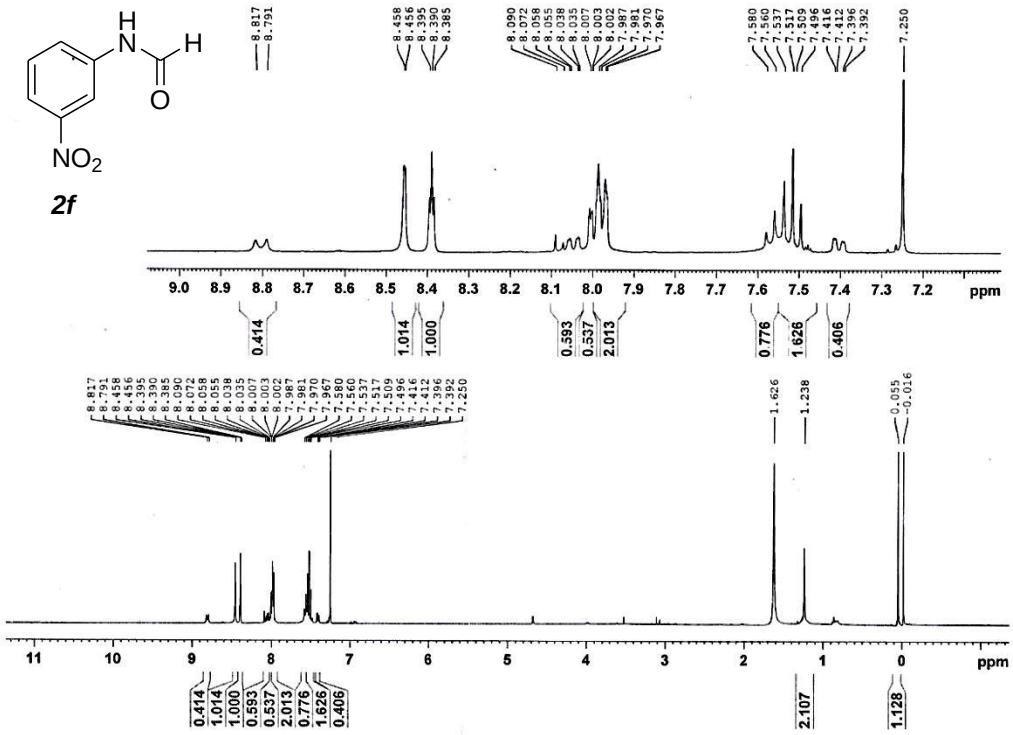
(Scheme 2, entry 2d)



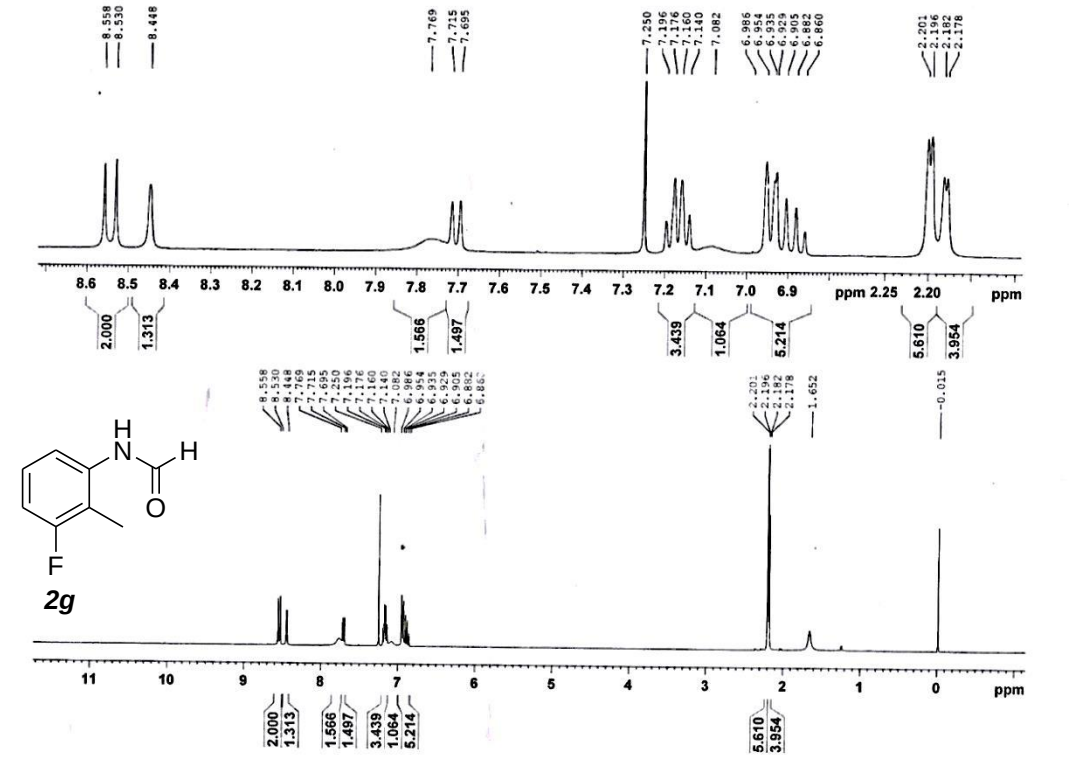
(Scheme 2, entry 2e)

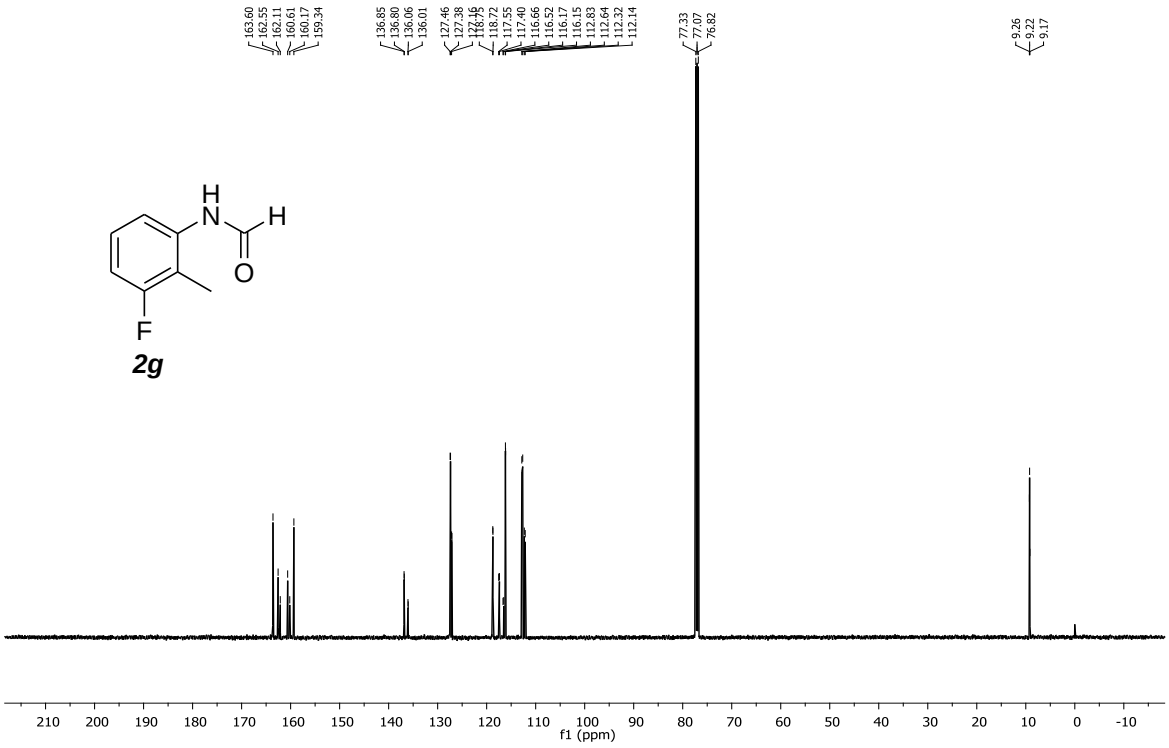


(Scheme 2, entry 2f)

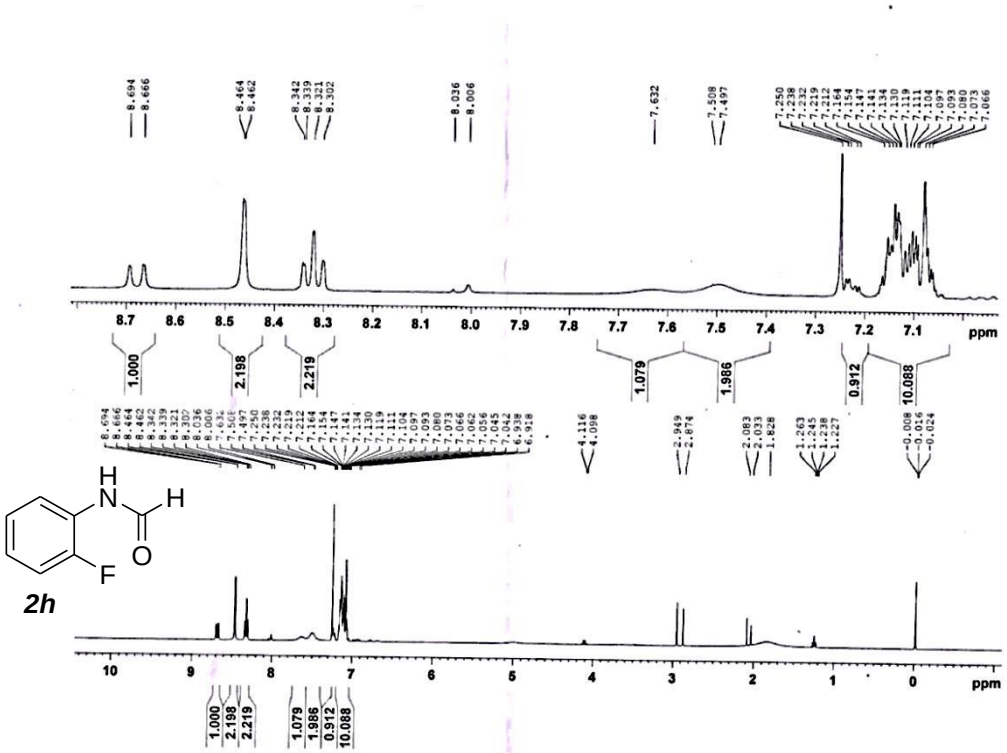


(Scheme 2, entry 2g)

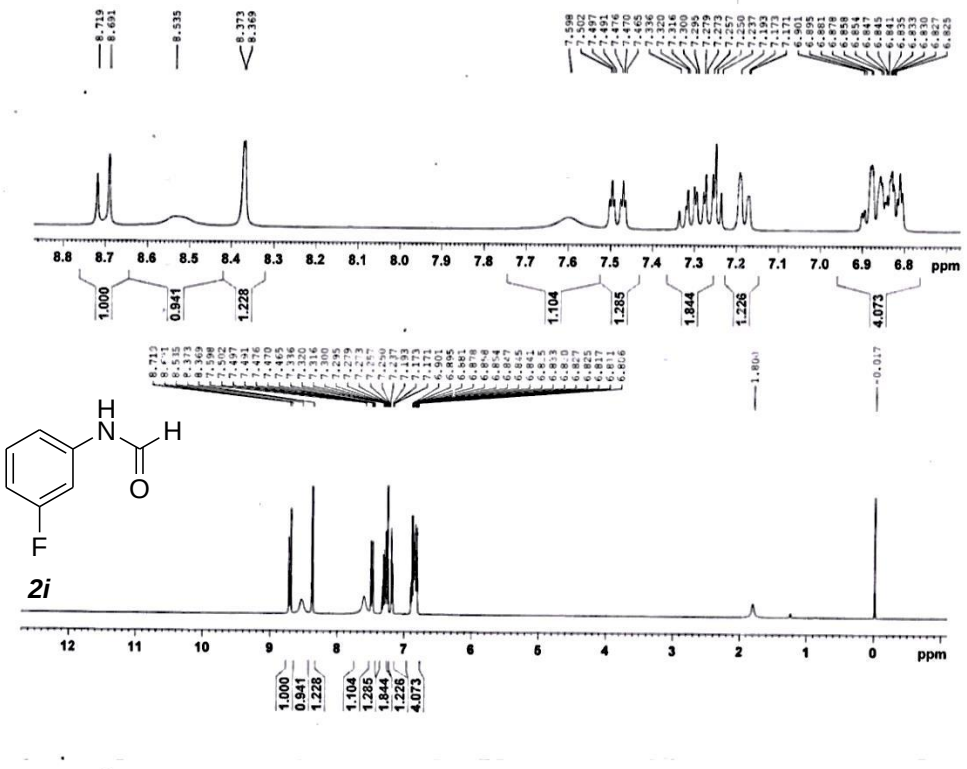




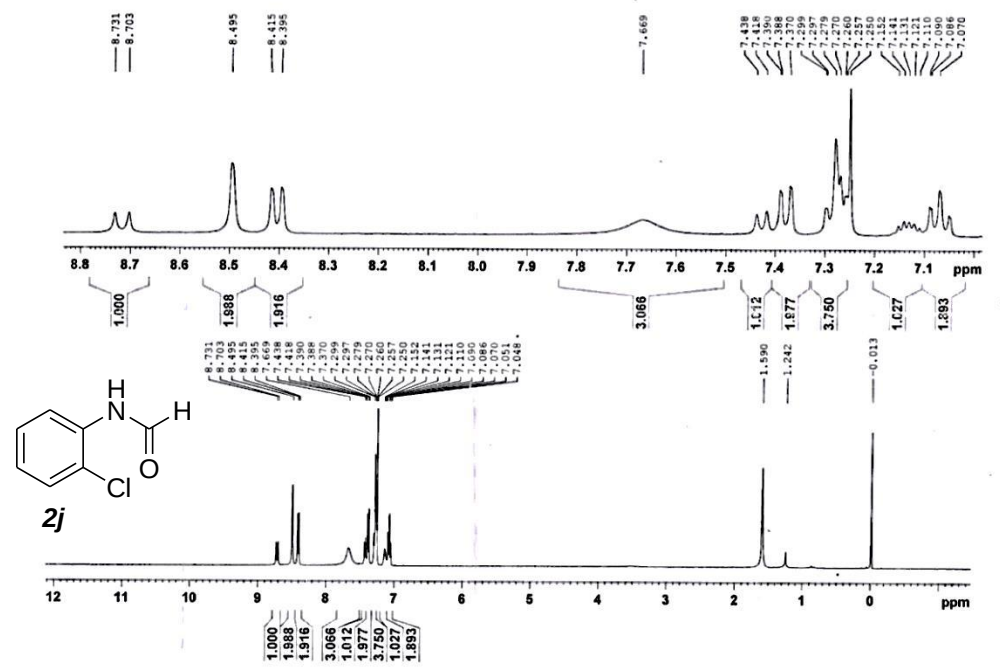
(Scheme 2, entry 2h)



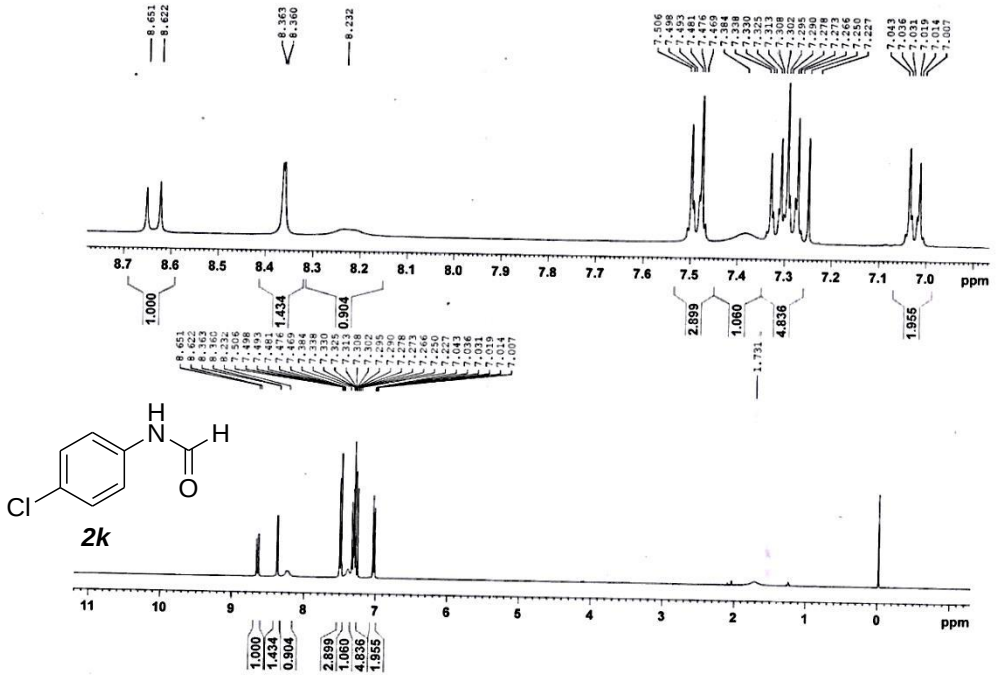
(Scheme 2, entry 2i)



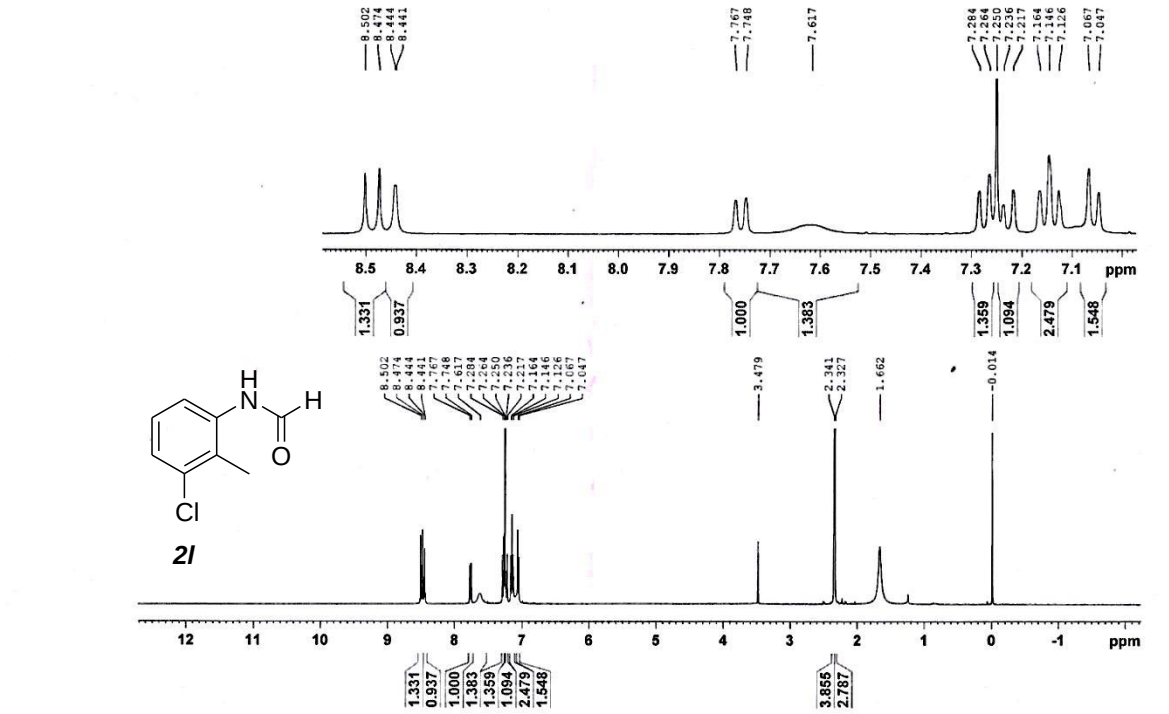
(Scheme 2, entry 2j)

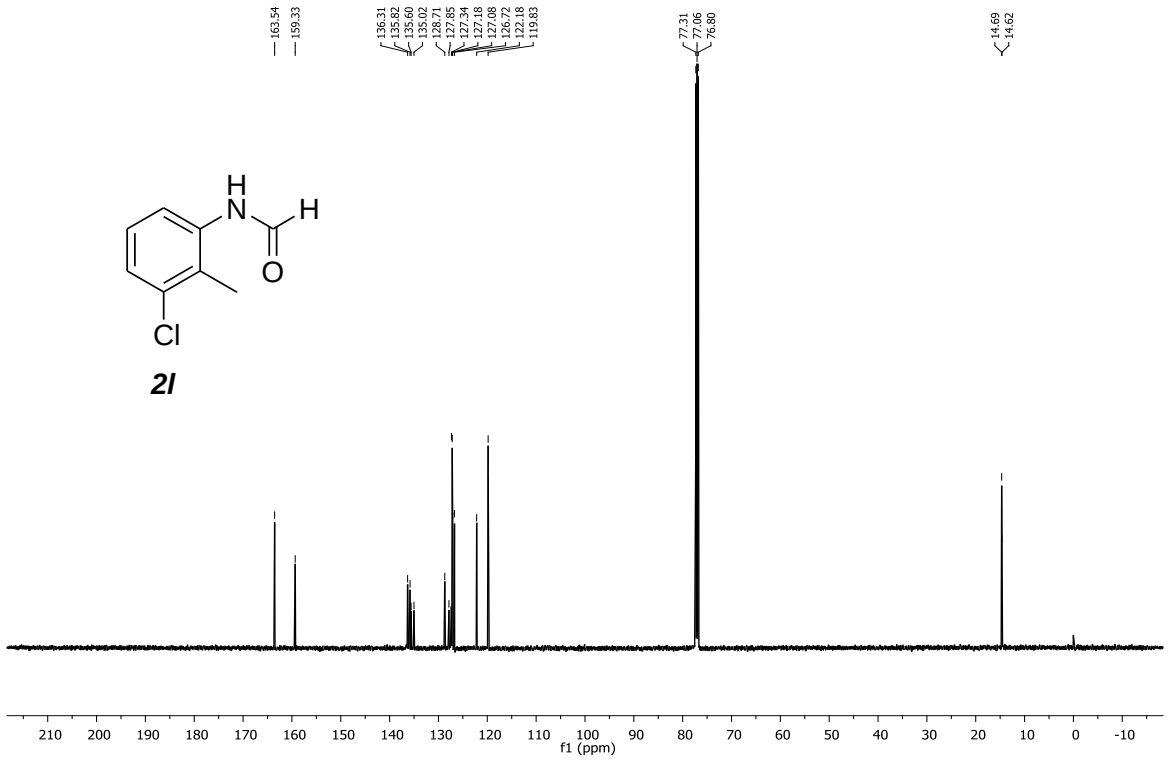


(Scheme 2, entry 2k)

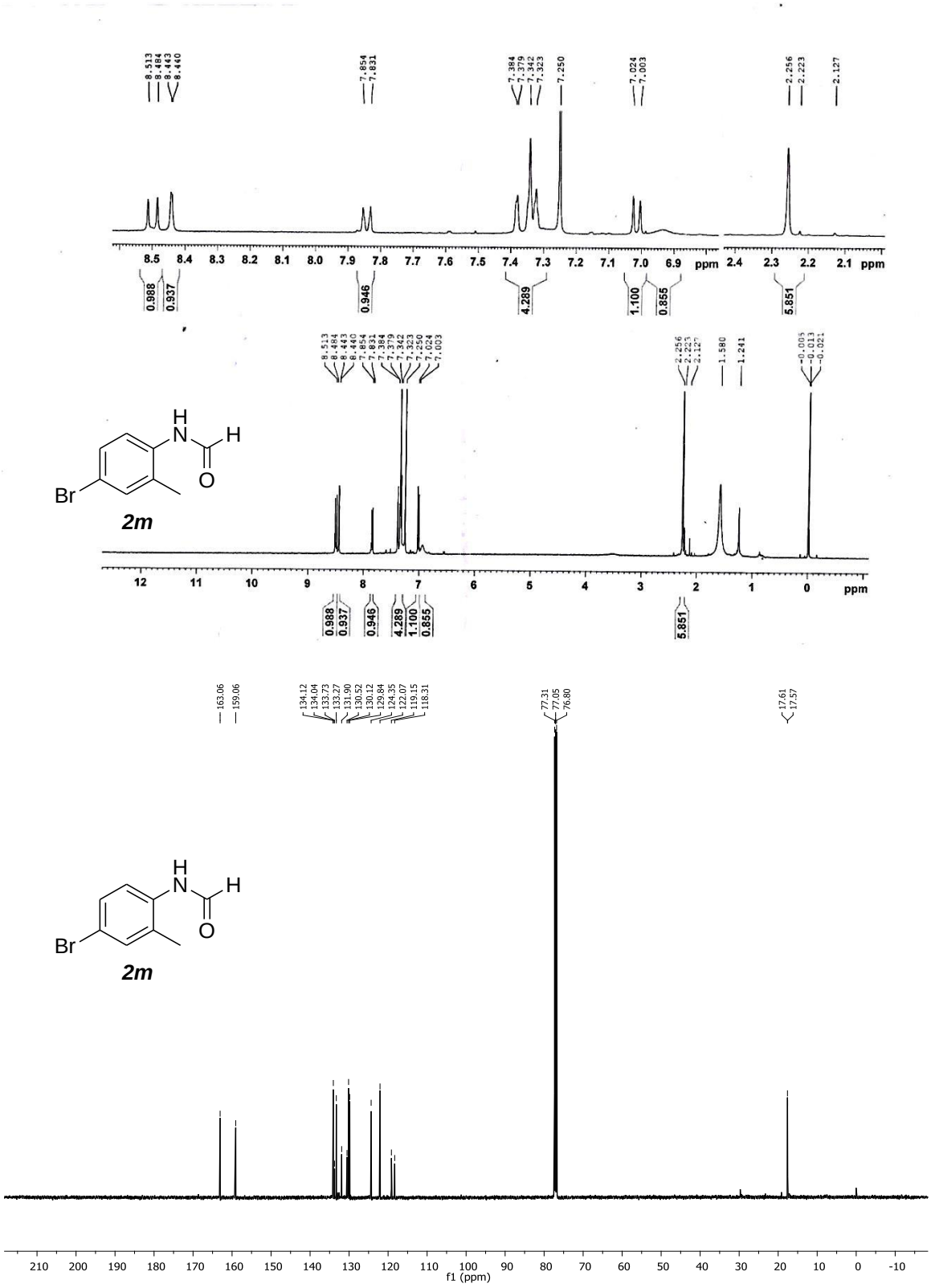


(Scheme 2, entry 2l)

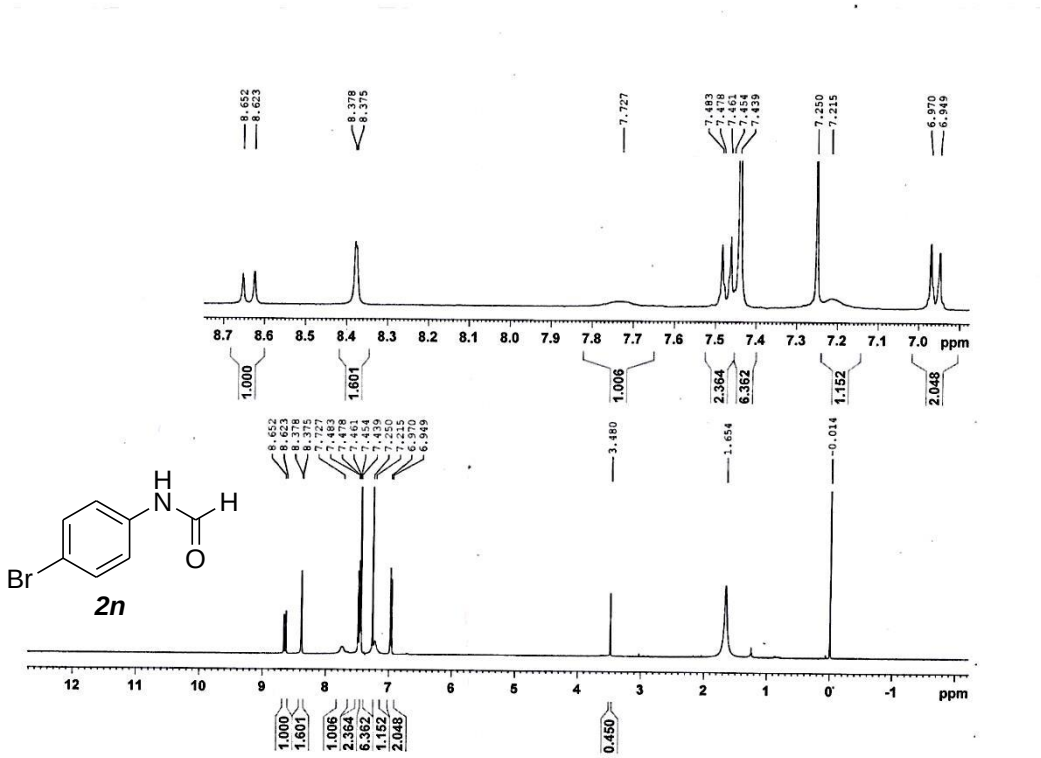




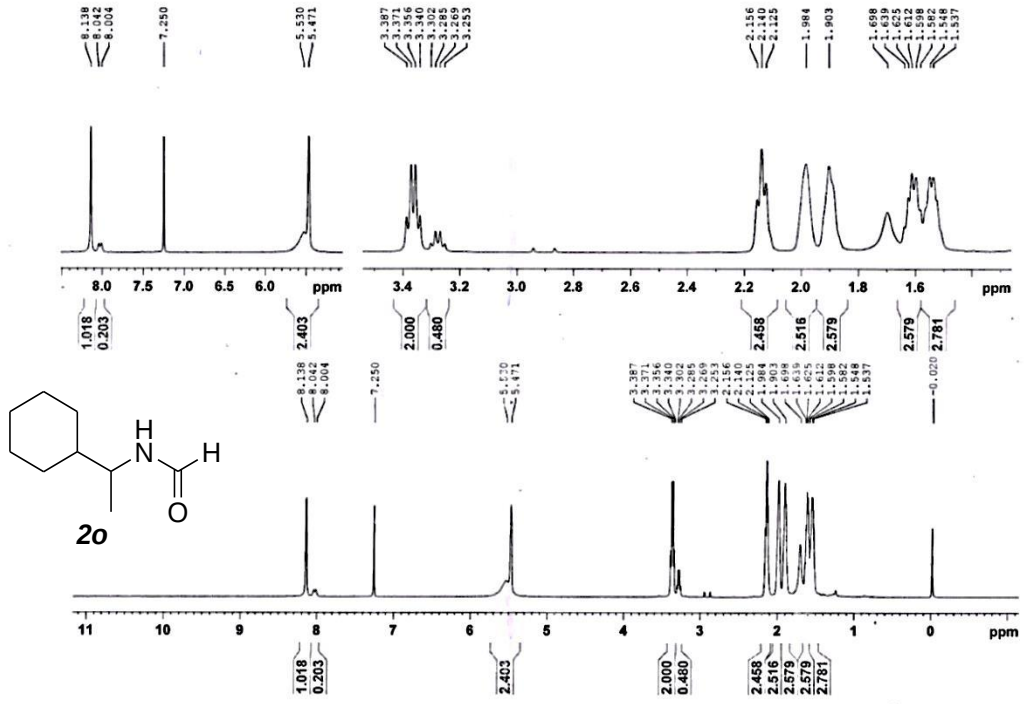
(Scheme 2, entry 2m)



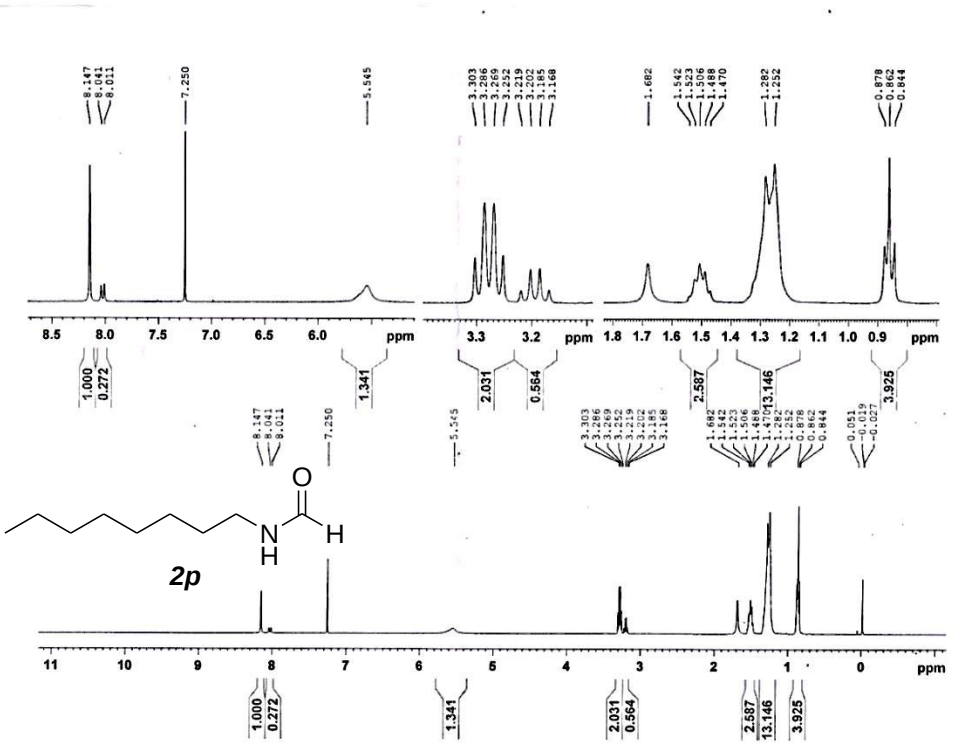
(Scheme 2, entry 2n)



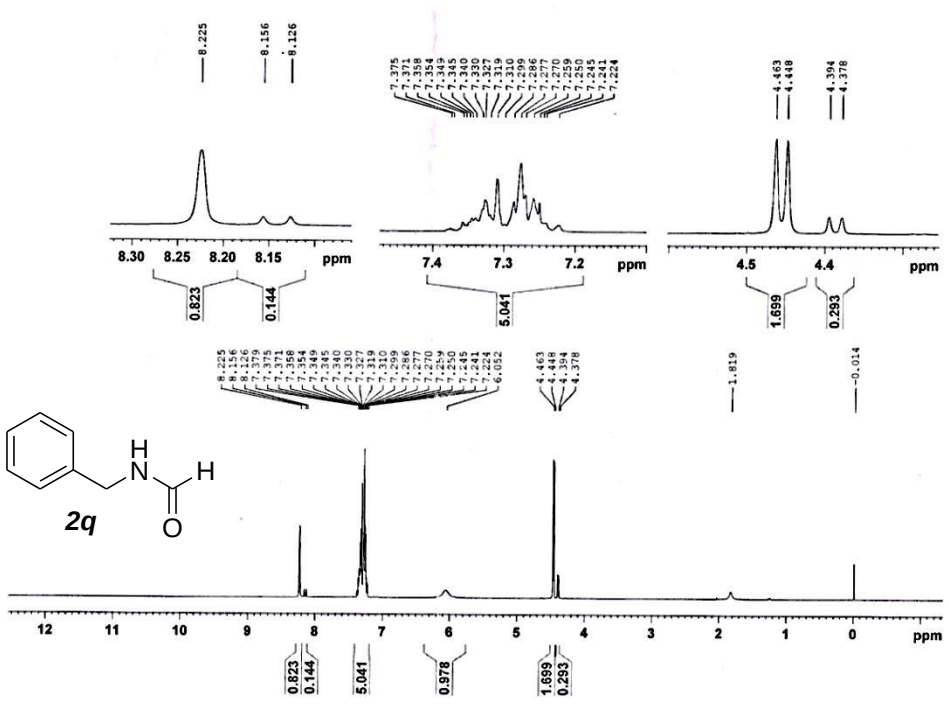
(Scheme 2, entry 2o)



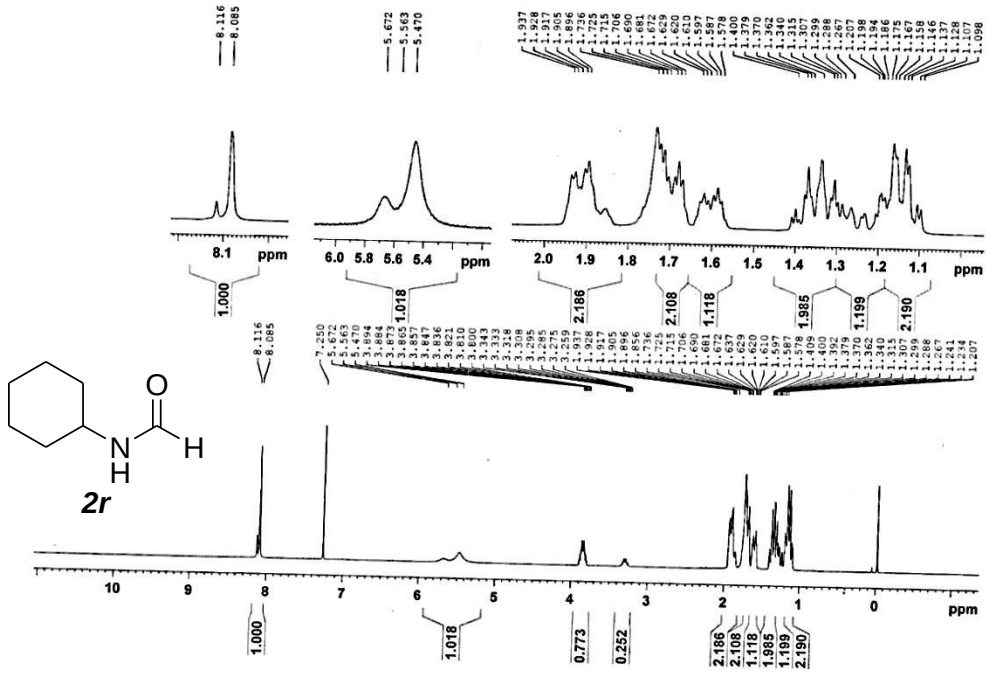
(Scheme 2, entry 2p)



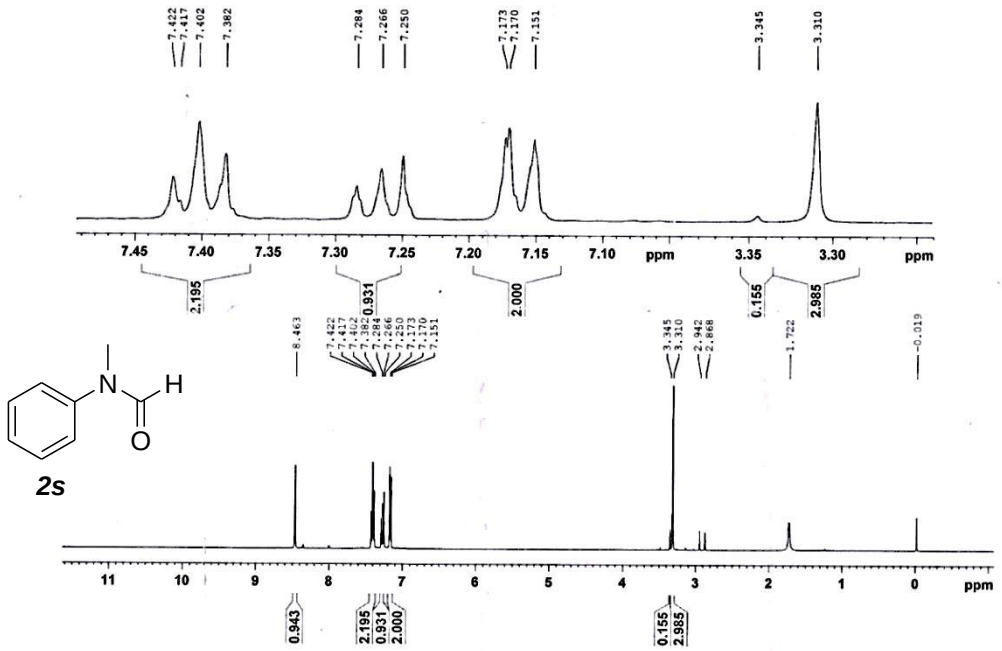
(Scheme 2, entry 2q)



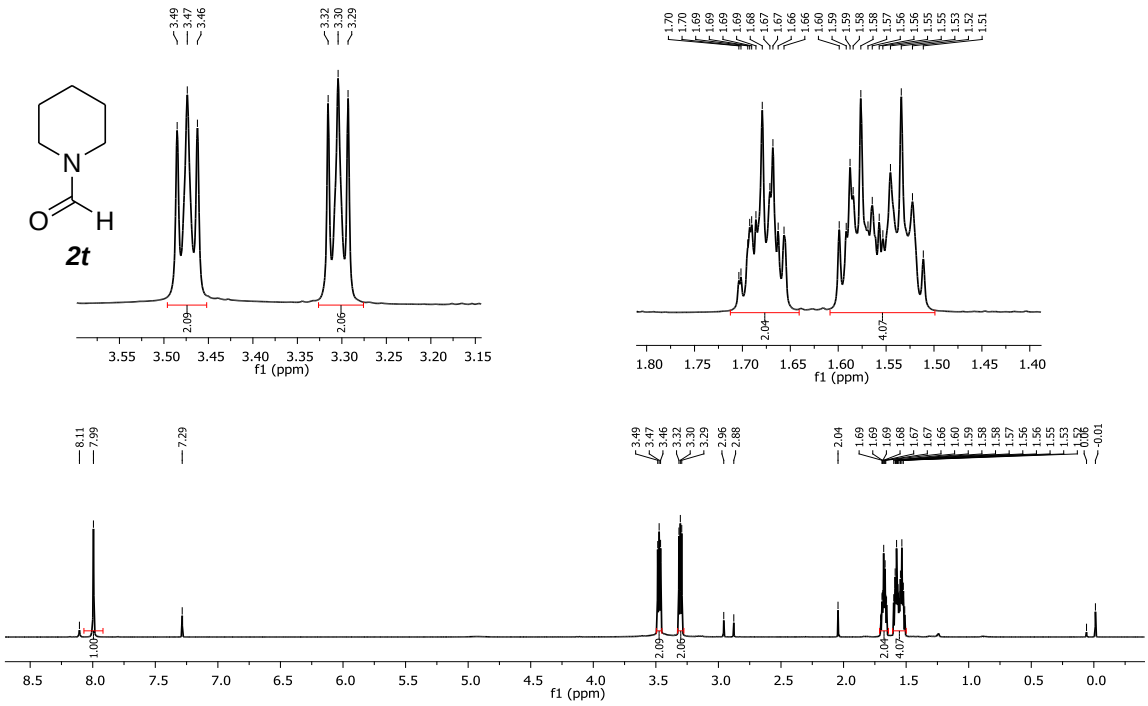
(Scheme 2, entry 2r)



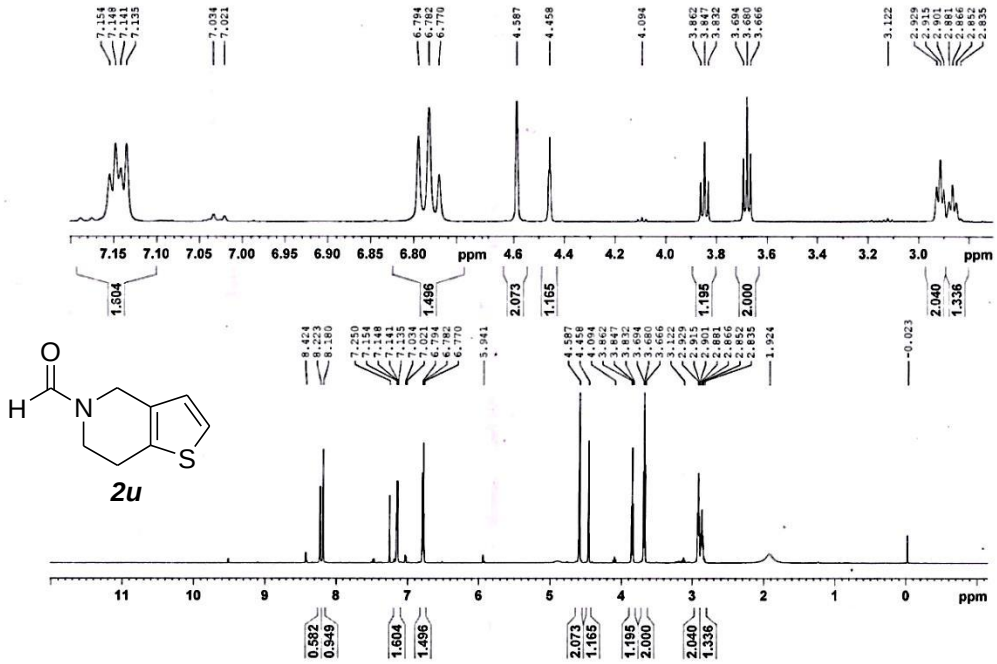
(Scheme 2, entry 2s)

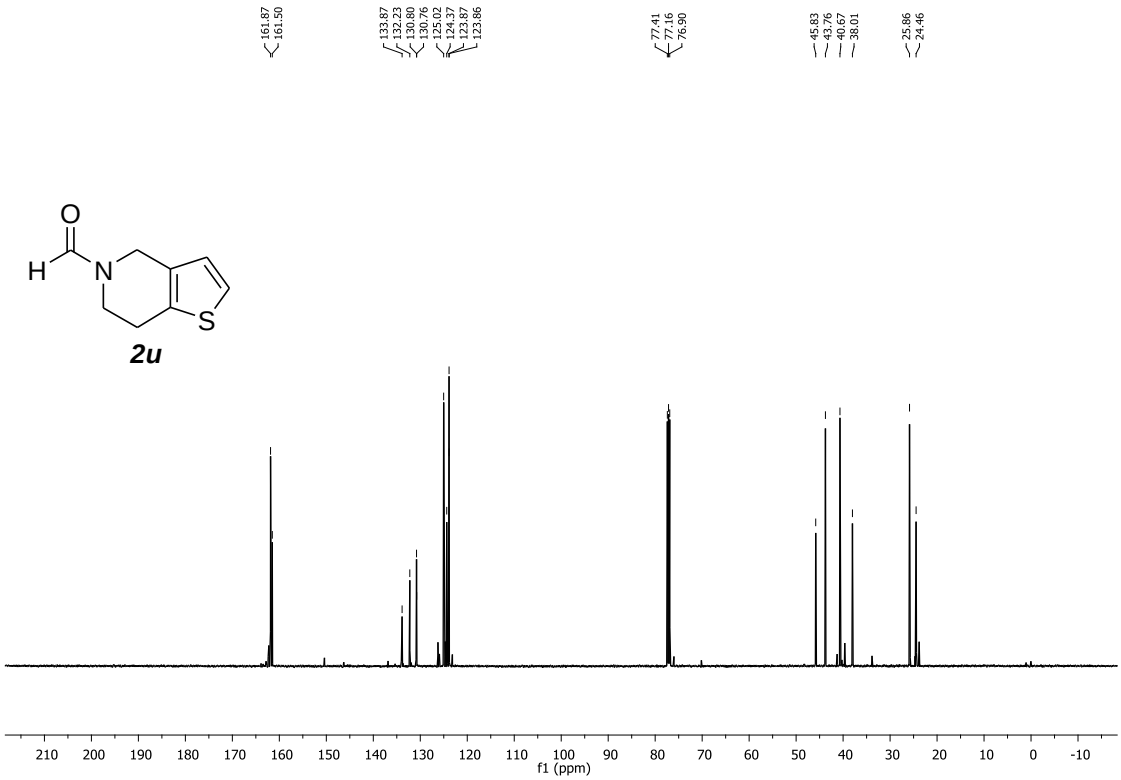


(Scheme 2, entry 2t)

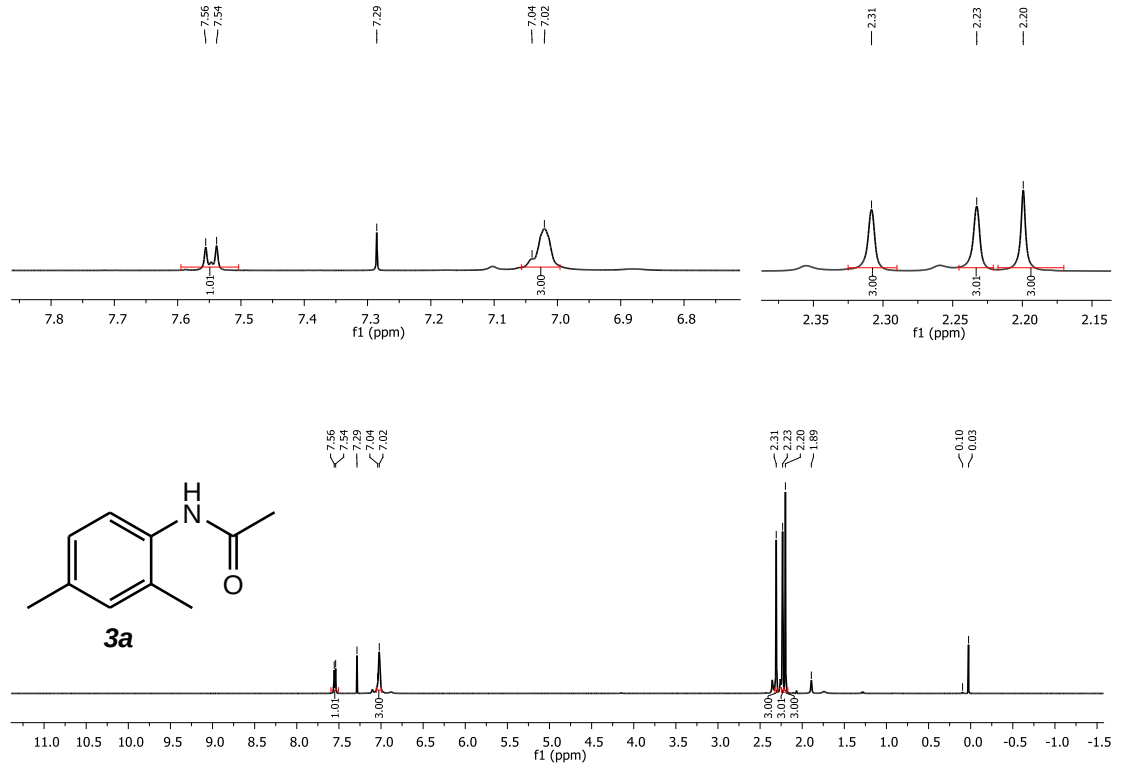


(Scheme 2, entry 2u)

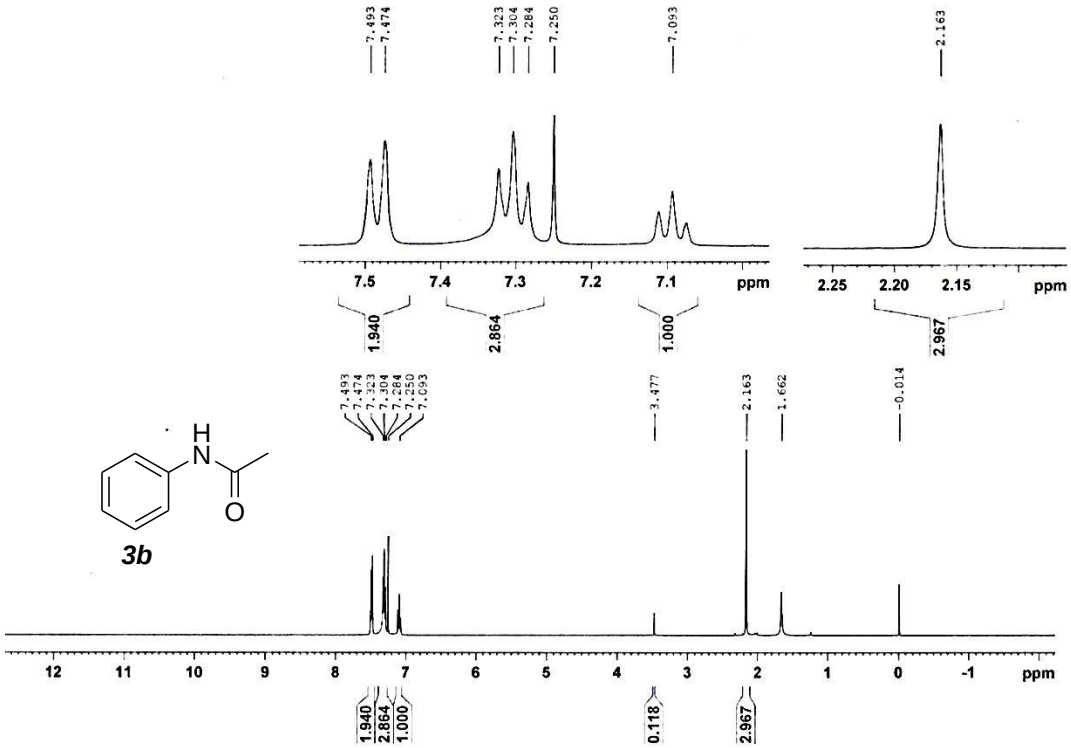




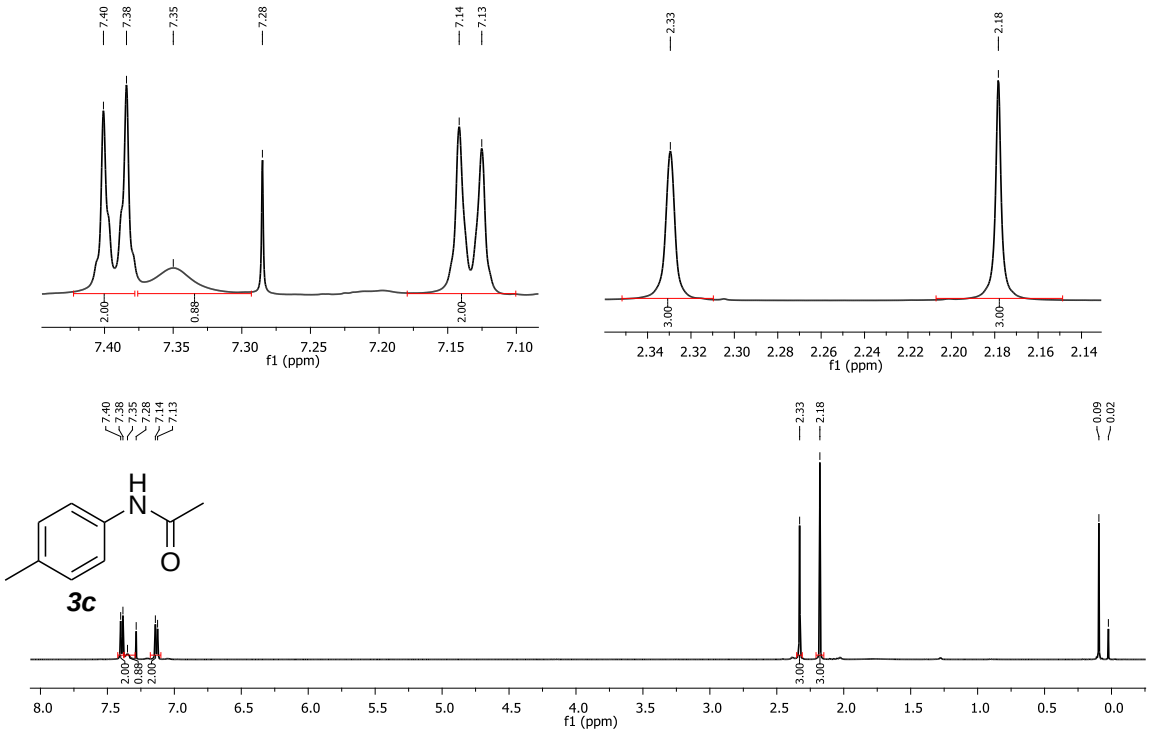
(Scheme 3, entry 3a)



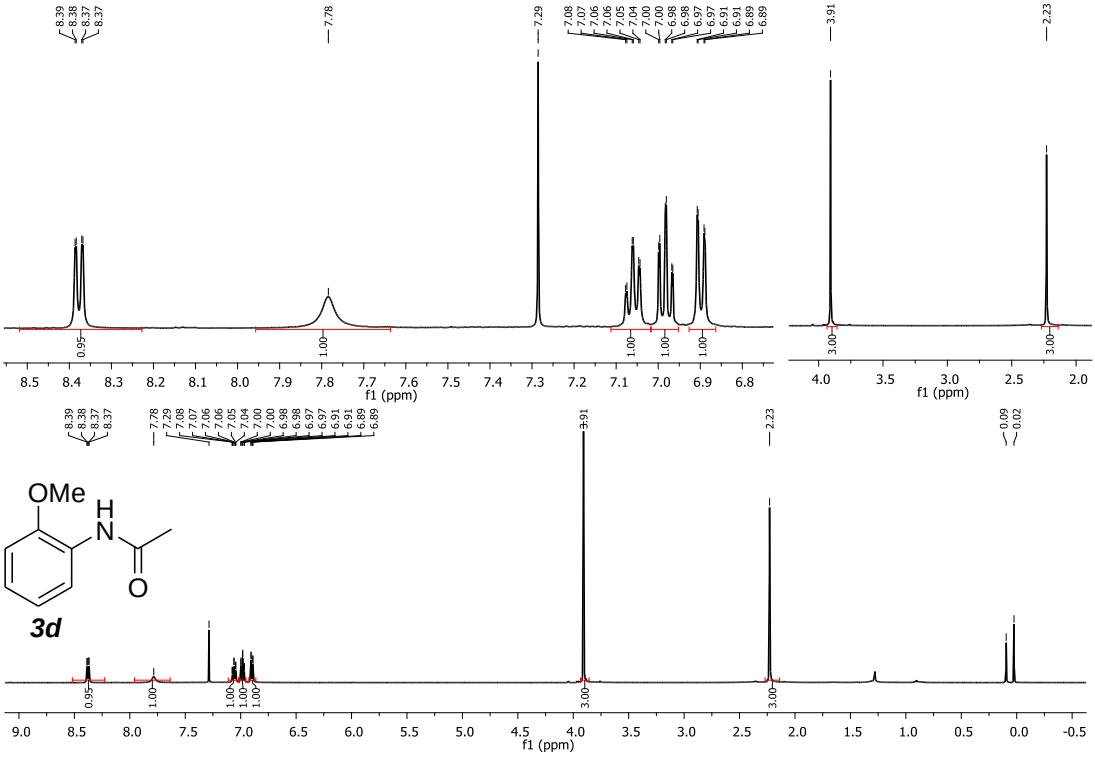
(Scheme 3, entry 3b)



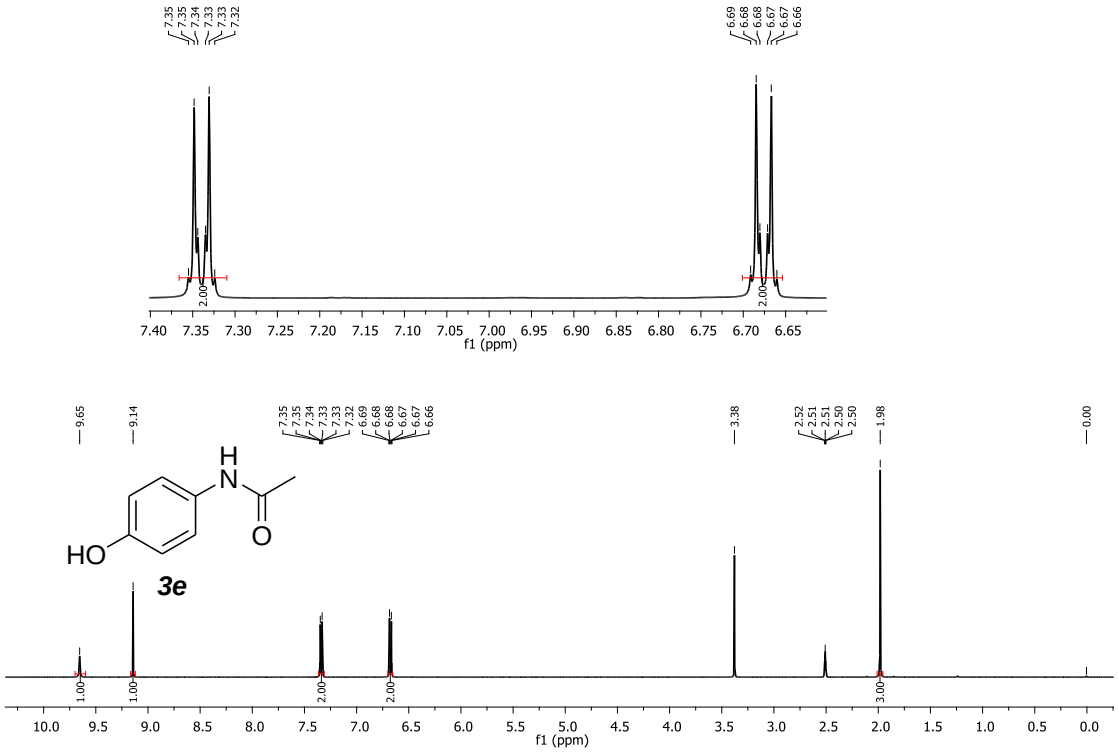
(Scheme 3, entry 3c)



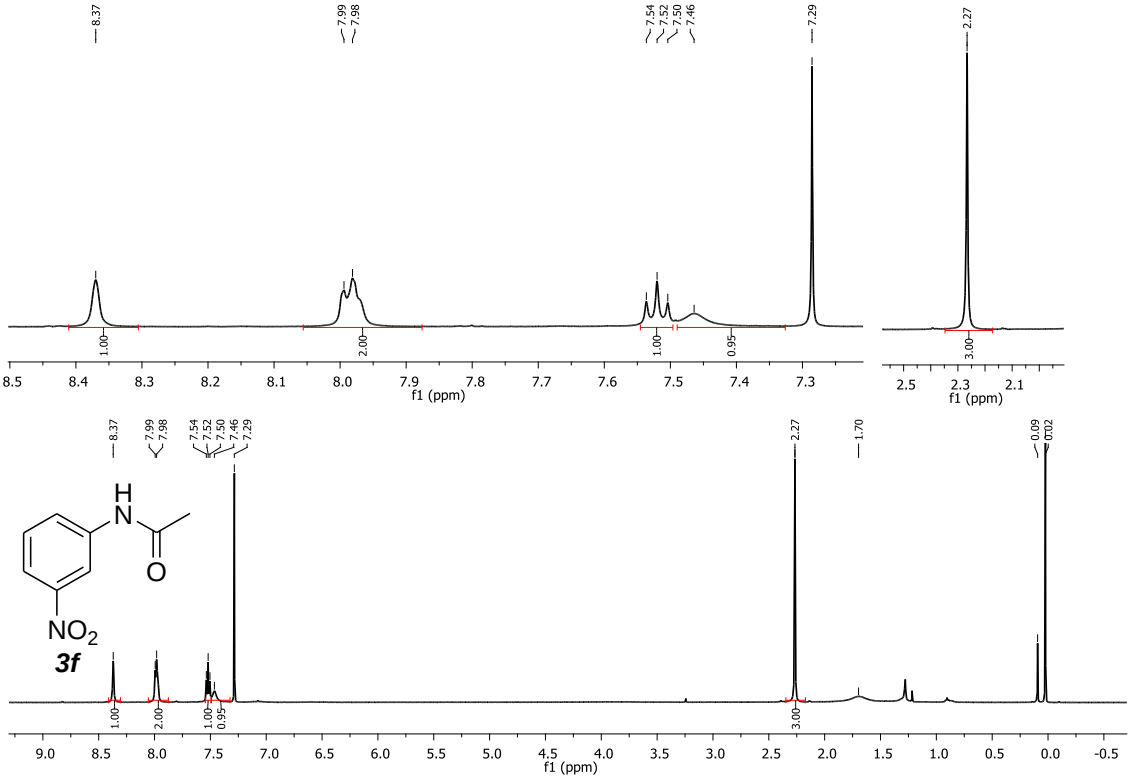
(Scheme 3, entry 3d)



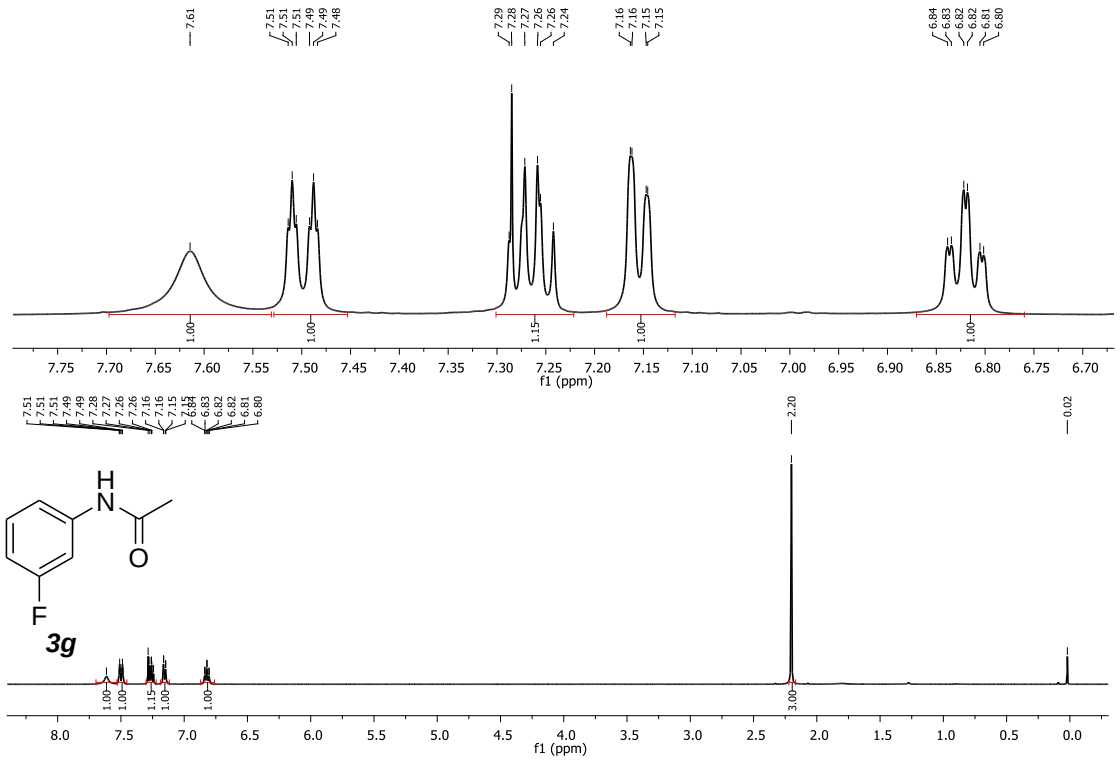
(Scheme 3, entry 3e)



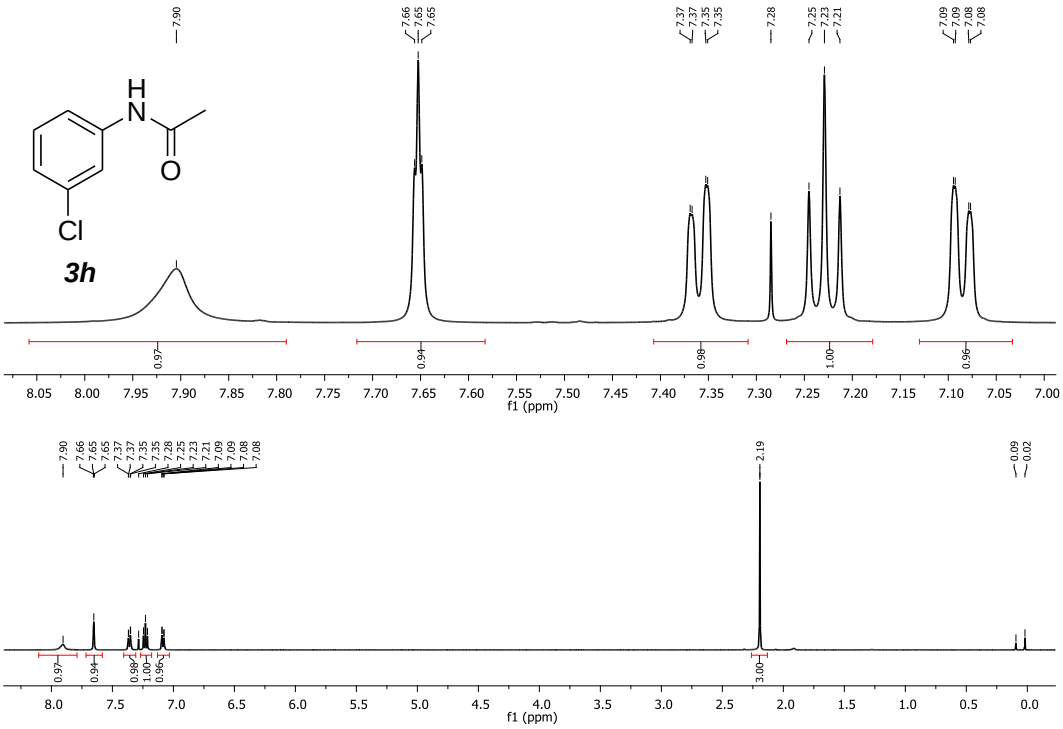
(Scheme 3, entry 3f)



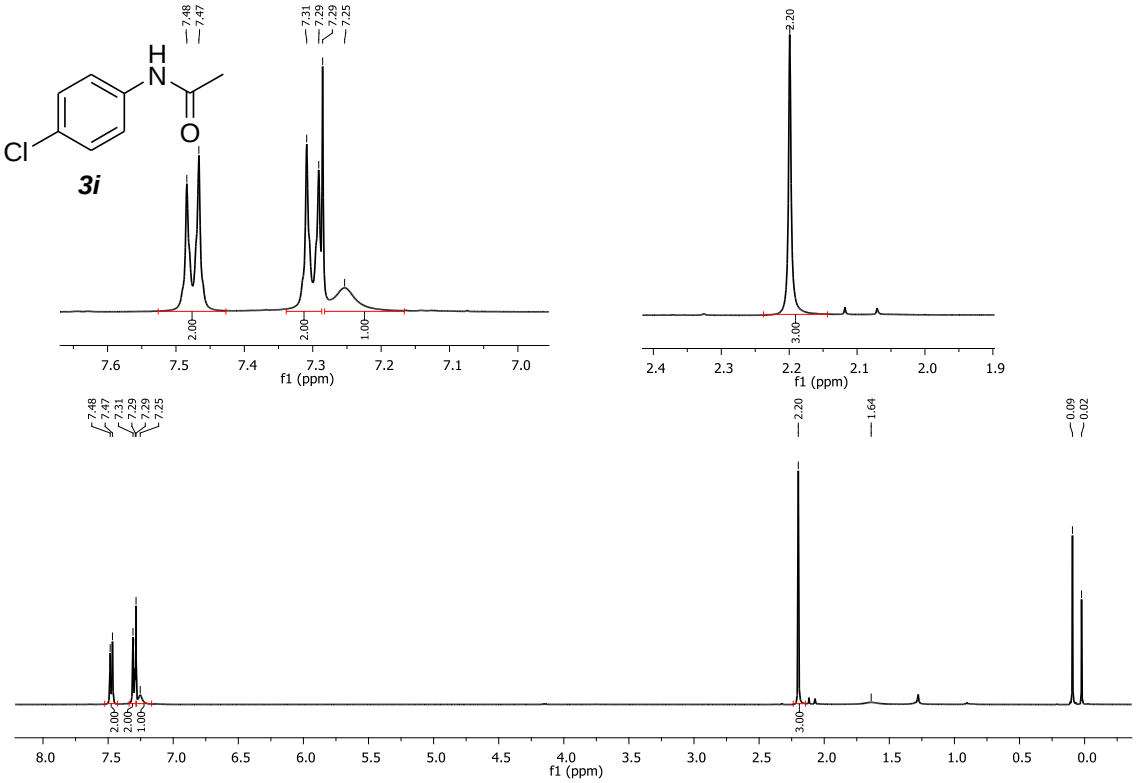
(Scheme 3, entry 3g)



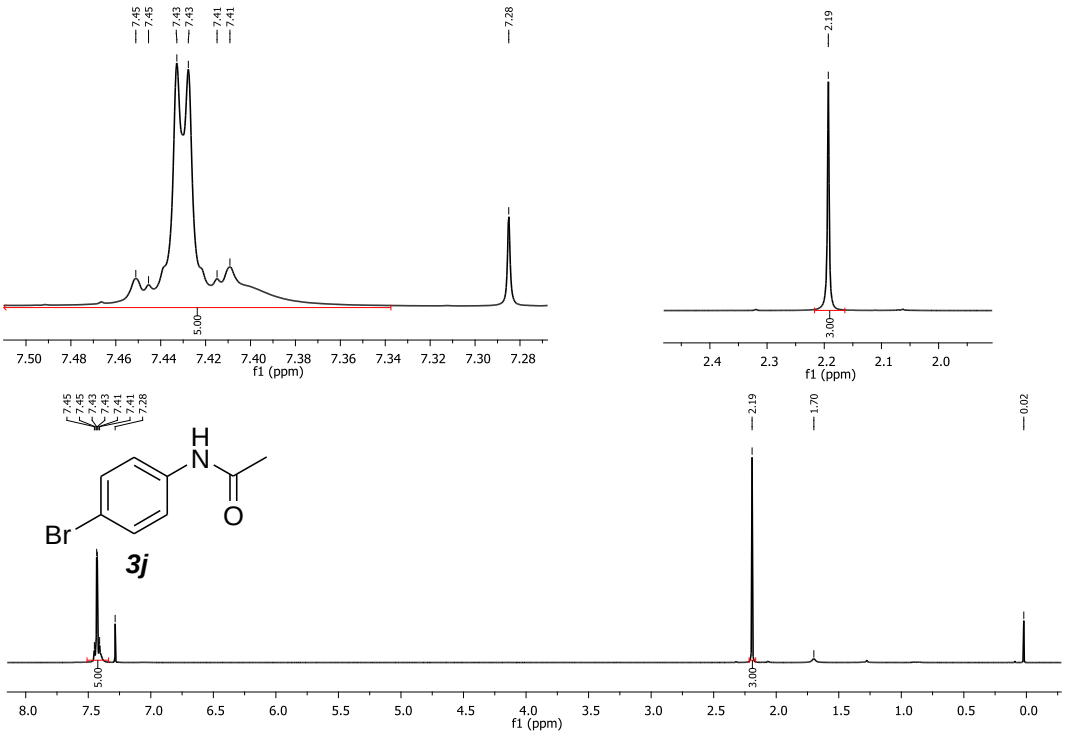
(Scheme 3, entry 3h)



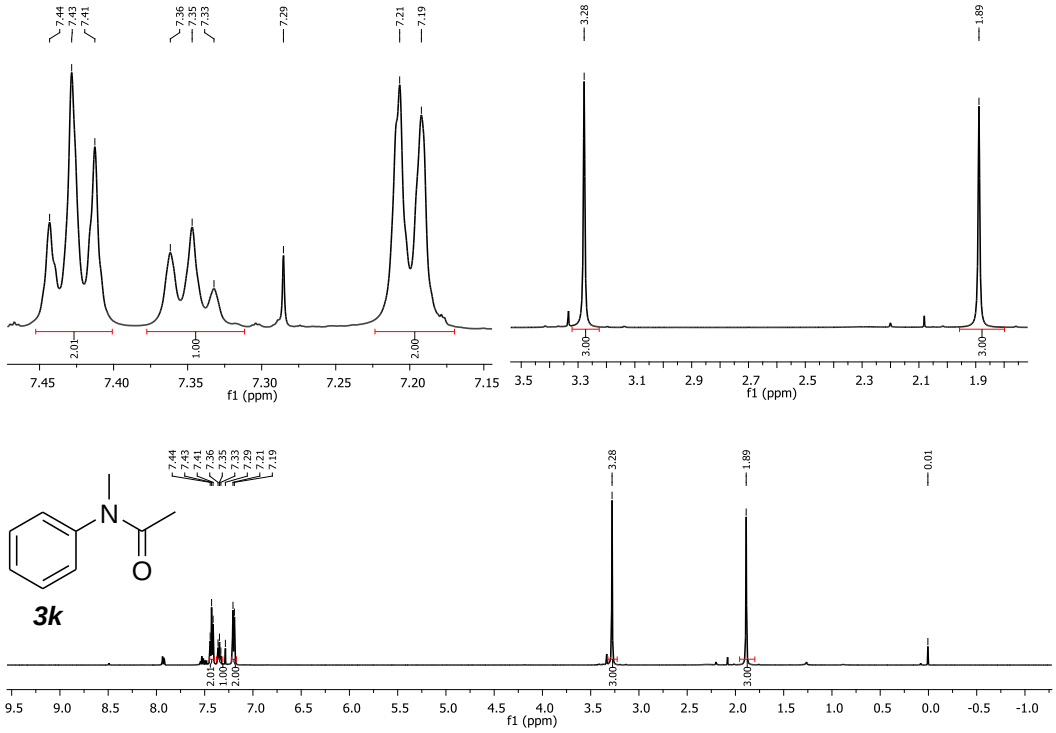
(Scheme 3, entry 3i)



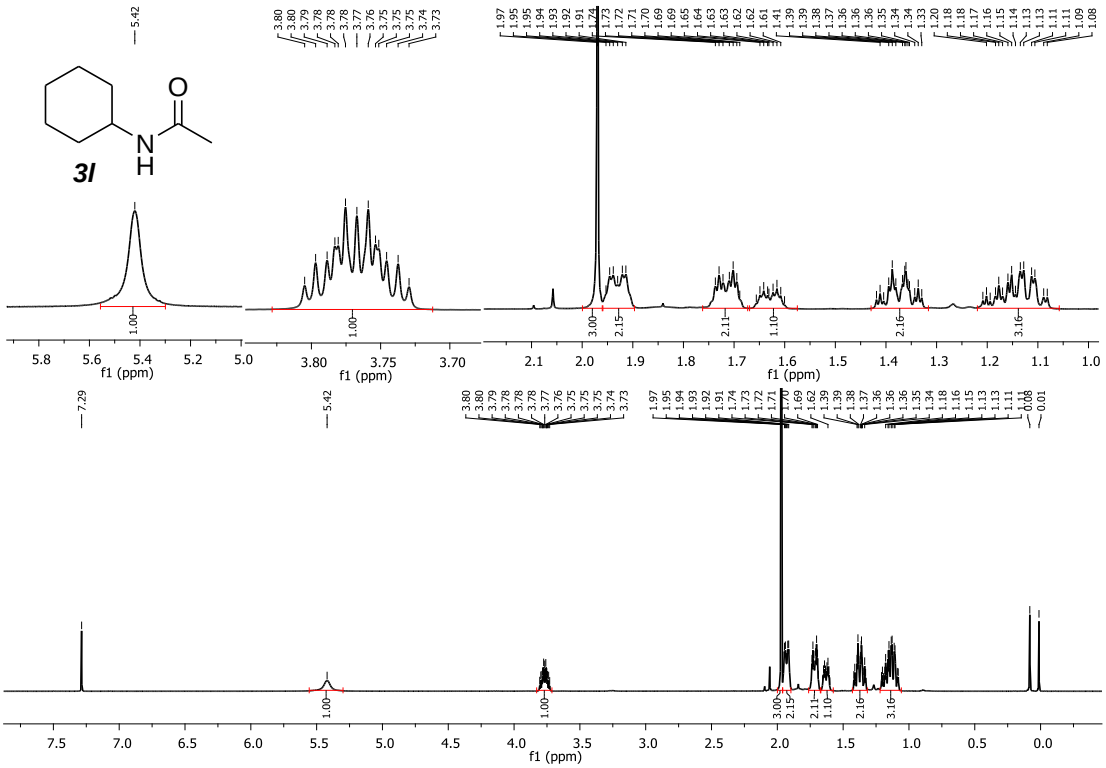
(Scheme 3, entry 3j)



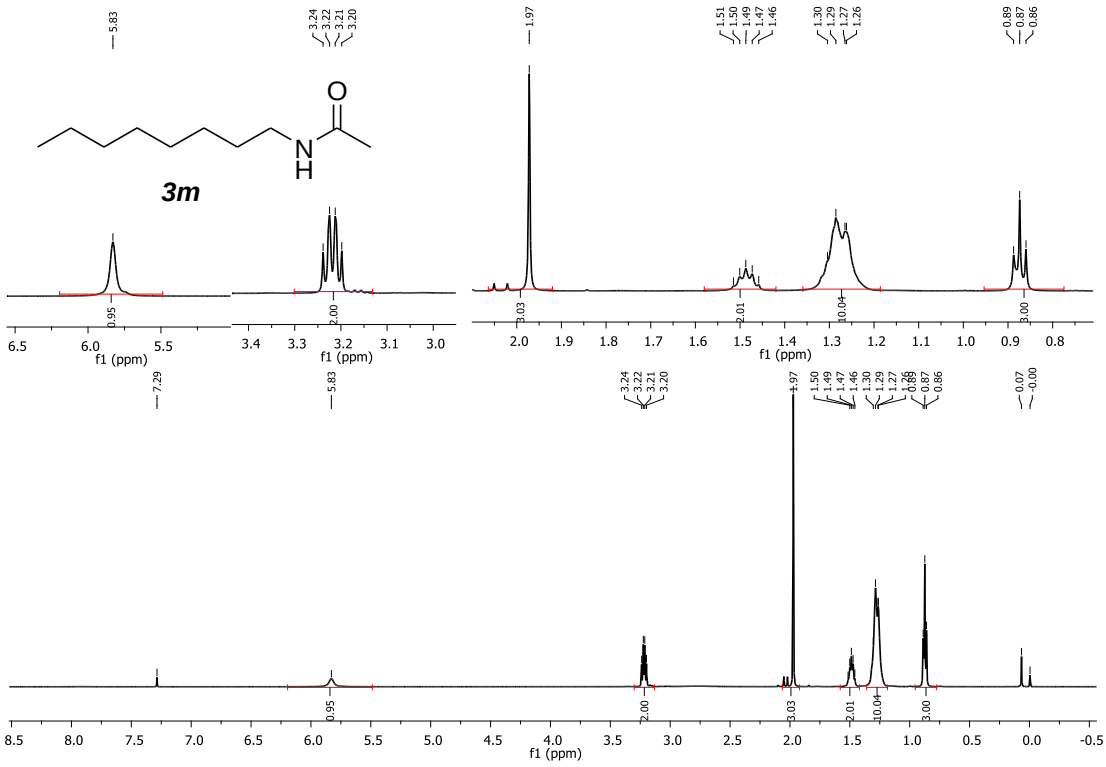
(Scheme 3, entry 3k)



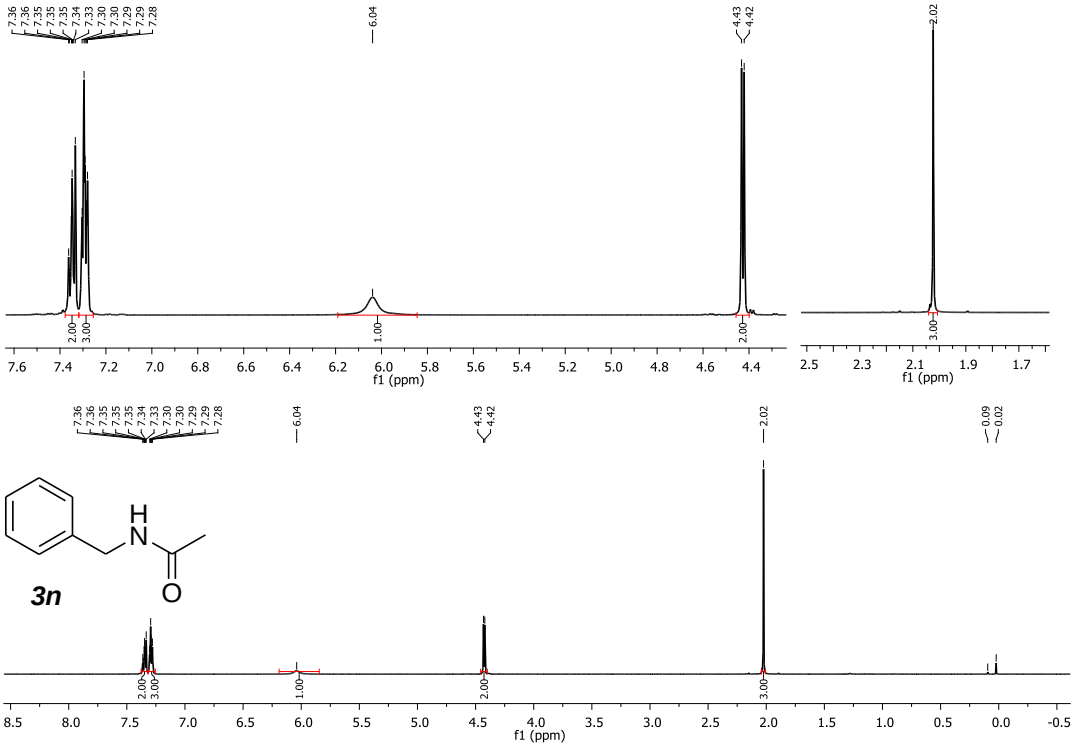
(Scheme 3, entry 3l)



(Scheme 3, entry 3m)

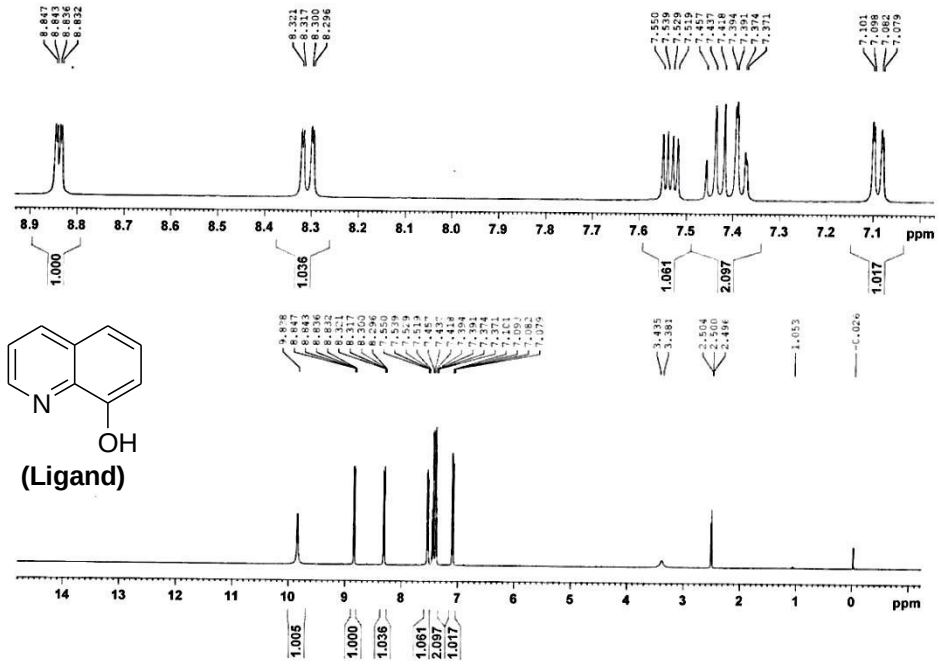


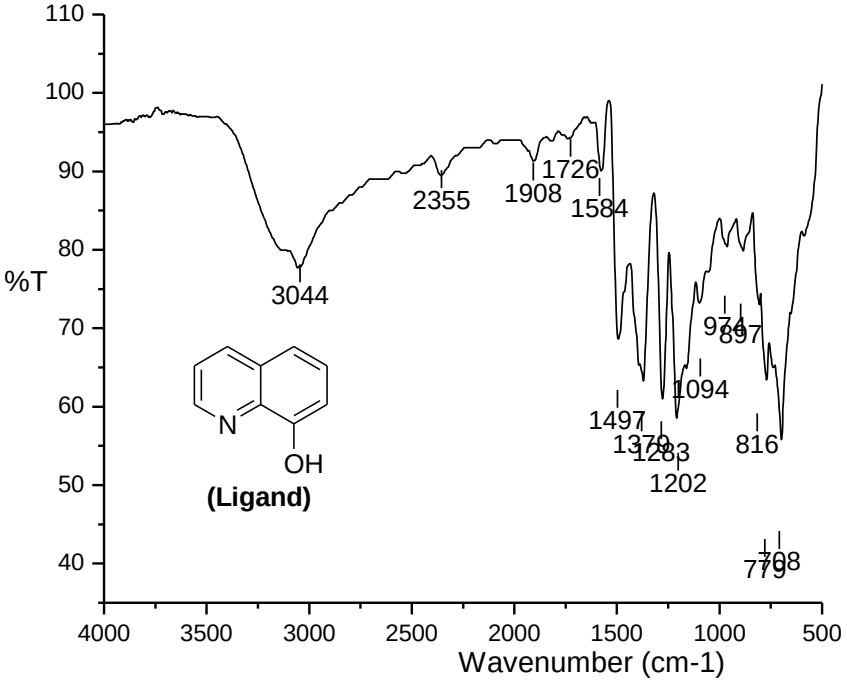
(Scheme 3, entry 3n)



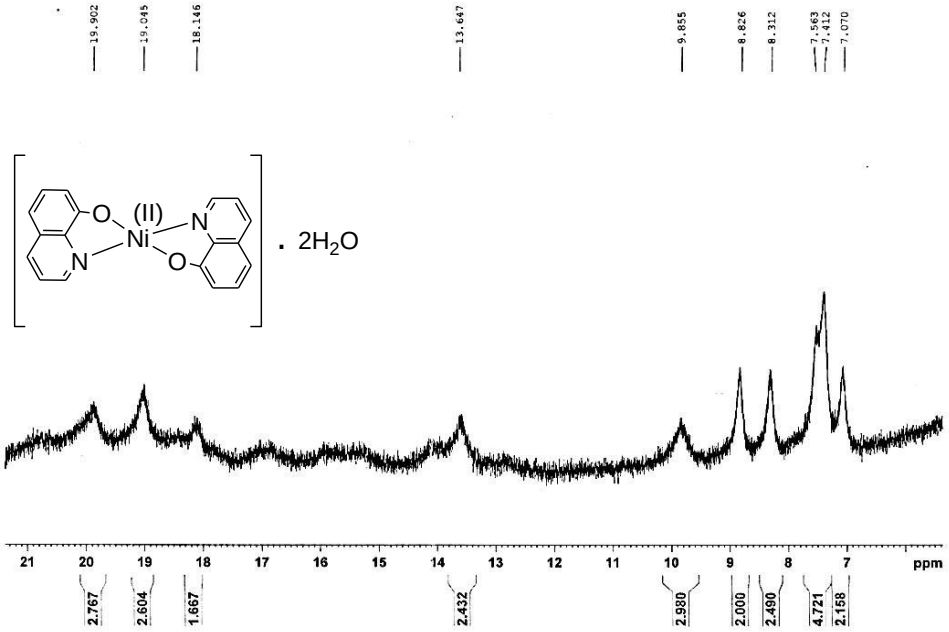
7. NMR and IR spectra of ligand and catalyst [Ni(quin)$_2$]

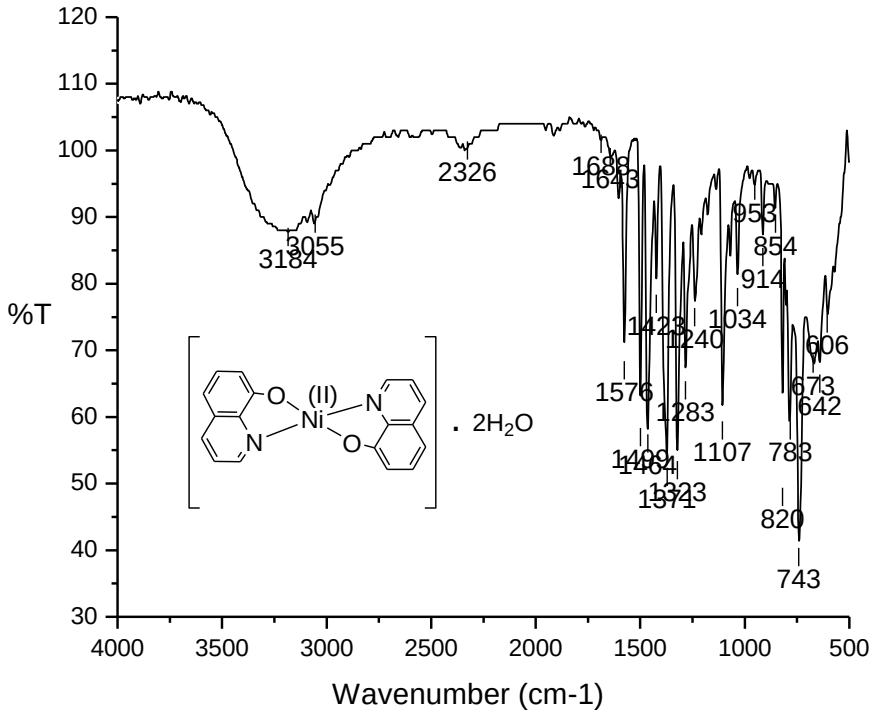
(Ligand)



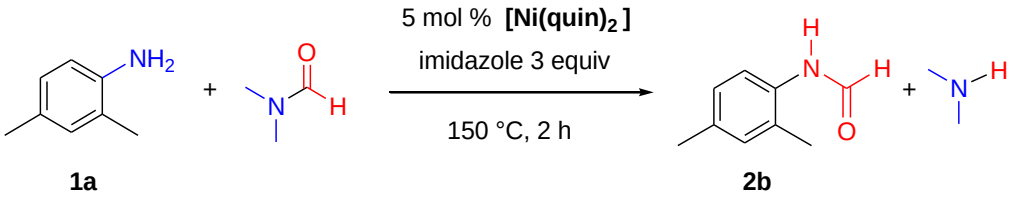


[Ni(quin)$_2$] Catalyst

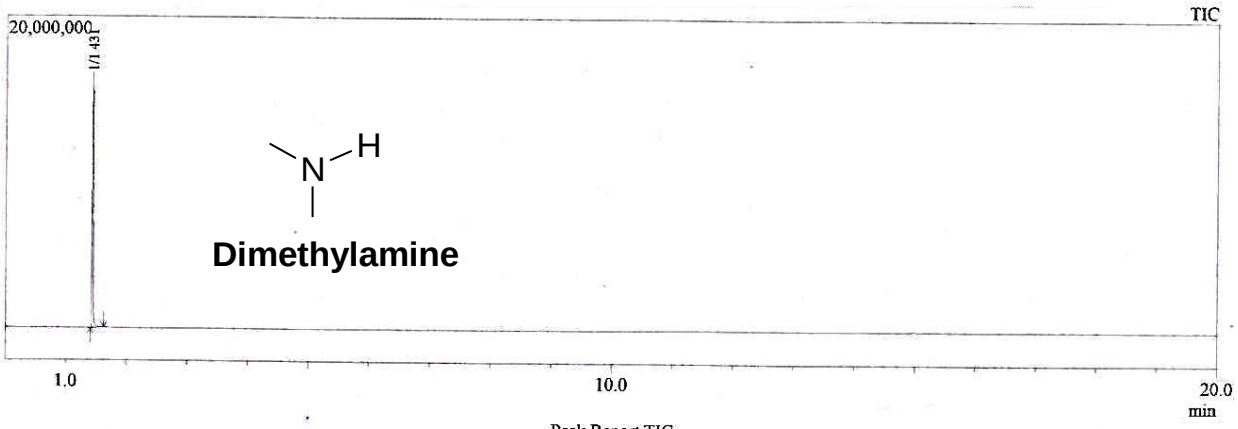




8. GC-MS of amine gas evolved during reaction (Support for DMF as formyl source)



1a **2b**

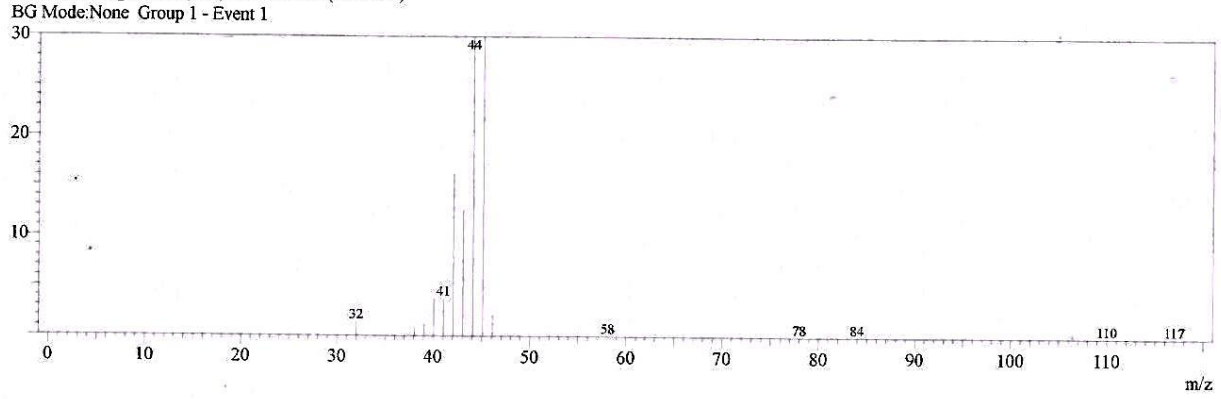


Peak Report TIC

Peak#	Name	R.Time	Area	Area%	Base m/z
1	Dimethylamine	1.43	20518978	100.00	44
			20518978	100.00	

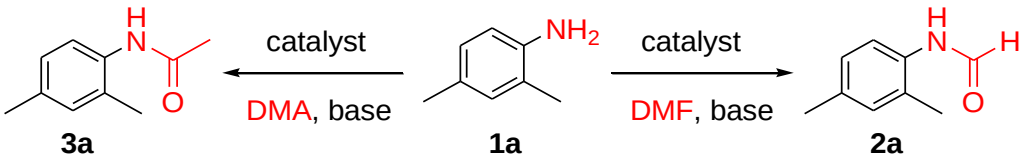
Spectrum

Line#:1 R.Time:1.440(Scan#:289)
MassPeaks:446
RawMode:Single 1.440(289) BasePeak:44(4268959)
BG Mode:None Group 1 - Event 1



9. Optimization table

Selected observations during reaction optimization[a]

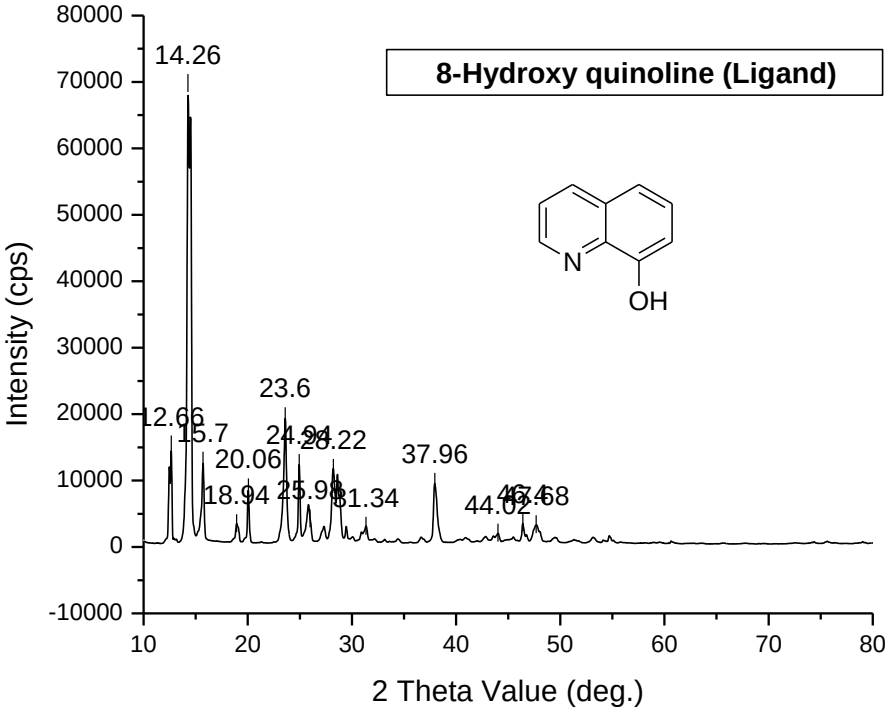


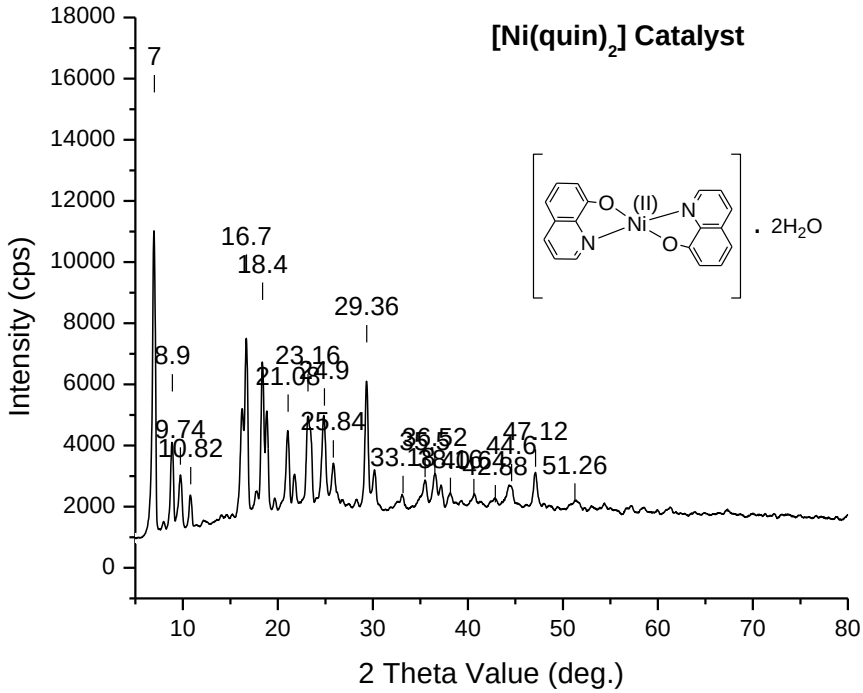
3a **1a** **2a**

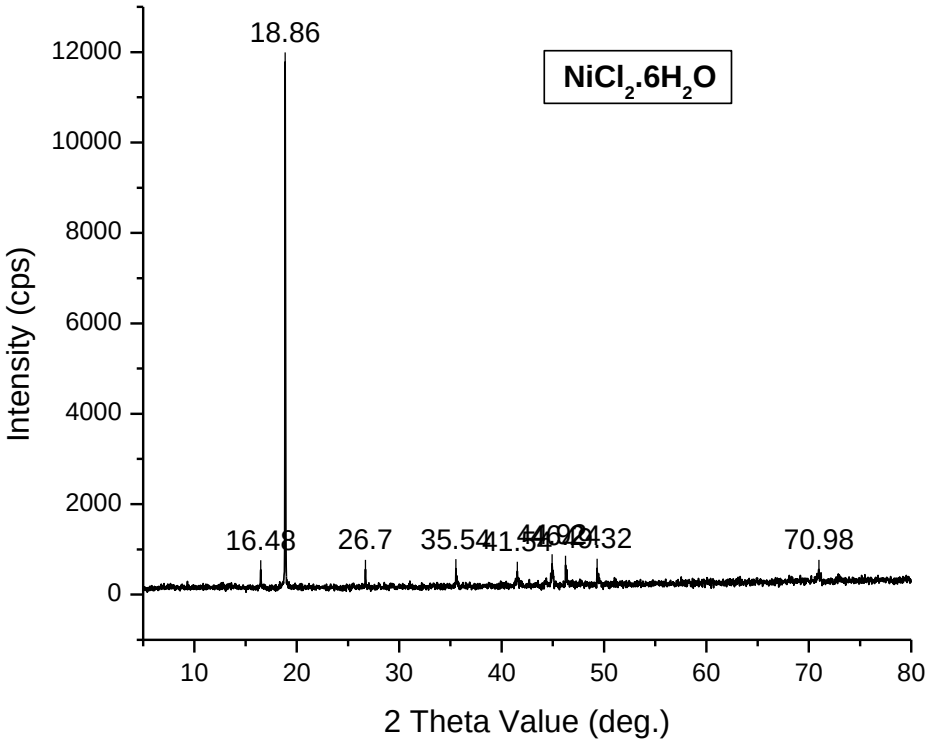
entry	substrate	catalyst (mol %)	base (equiv)	reagent (equiv) / solvent (ml)	temp (°c)	time (h)	**2a** yield[b] (%)
1	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	TEA (3)	----- / DMF (2.5)	150	24	25
2	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	DABCO (3)	----- / DMF (2.5)	150	24	25
3	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	2,6-lutidine (2)	----- / DMF (2.5)	150	24	28
4	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	NaOCOCH3 (3)	----- / DMF (2.5)	150	24	35
5	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	KOtBu (2)	----- / DMF (2.5)	150	24	55
6	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	NaOMe (5)	----- / DMF (2.5)	150	24	60
7[c, d]	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	NaH (1.5)	DMF(2)/ THF (2.5)	70	24	65
8	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	imidazole (3)	----- / DMF (5)	150	24	68
9	2,4-dimethylaniline	-----	imidazole (3)	----- / DMF (2.5)	150	24	6
10	2,4-dimethylaniline	$[Ni(quin)_2]$ (1)	imidazole (3)	----- / DMF (2.5)	150	24	20
11[e]	-----	$[Ni(quin)_2]$ (5)	imidazole (1)	----- / DMF (2.5)	150	24	Nil[k]
12[f]	2,4-dimethylaniline	Cu Powder (5)	imidazole (3)	----- / DMF (2.5)	150	24	6
13[g]	2,4-dimethylaniline	$[Ni(Cl_2).6H_2O]$ (5)	imidazole (3)	----- / DMF (2.5)	150	24	6
14[d]	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	imidazole (3)	DMF(2) / o-xylene (2.5)	150	24	Nil
15[d]	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	imidazole (3)	DMF(2) / 1,4-Dioxane (2.5)	150	24	Nil
16[h]	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	imidazole (3)	----- / DMF (2.5)	80	24	Nil
17[i]	2,4-dimethylaniline	$[Ni(quin)_2]$ (5)	imidazole (3)	----- / DMF (2.5)	120	24	40
18[j]	**2,4-dimethylaniline**	**$[Ni(quin)_2]$ (5)**	**imidazole (3)**	**----- / DMF (2.5)**	**150**	**2**	**96**
19[j]	2,4-dimethylaniline	$[Ni(quin)_2]$ (10)	imidazole (3)	----- / DMF (2.5)	150	2	96

[a]All reactions were carried out on approximately a 0.5 g scale using 2,4-dimethylaniline (**1a)** (4.13 mmol, 1 equiv), solvent (2.5 mL, 5 volume), $[Ni(quin)_2]$ (**C1**) 1-10 mol %, base (1-5 equiv), temperature 150 °C for 24 h. All reagent and substrate addition was done at room temperature (25 °C). [b]Isolated yields. [c]Reaction temperature at 70 °C. [d]DMF (2 equiv). [e]Reaction carried out without **1a.** [f]Cu powder catalyst (**C2**). [g]$[NiCl_2.6H_2O]$ catalyst (**C3**). [h]Reaction temperature initially at ambient temperature then increased up to 50 °C and 80 °C. [i]Reaction temperature at 120 °C. [j]Reaction continued up to 2 h. [k]Not isolated, a product formed i.e. *N*-formyl imidazole is highly reactive towards water.

10. XRD of ligand (8-Hydroxyquinoline), catalyst [Ni(quin)$_2$] and [NiCl$_2$.6H$_2$O]






18.86
NiCl2.6H2O
12000
10000
8000
6000
4000
2000
0
Intensity (cps)
16.48
26.7
35.54
70.98
10
20
30
40
50
60
70
80
2 Theta Value (deg.)